Development and Application of Hollow Fiber Membranes Specialized in Direct Contact Membrane Distillation

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Kwon

Advisor
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Abstract

As a thermally driven process, membrane distillation (MD), has been investigated in application of the new technology for desalination process. Development in membrane market since 1980's, improvement and better understanding toward membrane have started to obtain the desired properties in membrane separation process. MD process obtains pure water from evaporation of feed volatile components through porous hydrophobic membrane. Furthermore, MD process shows the similar evaporation law compared to evaporation process, but benefits operation process in low temperature and high separation efficiency. For these reasons, membrane distillation (MD) process is considered as new technology in desalination. However, the MD process is not commercially implemented yet due to its relatively very low permeability compared RO process.

MD process has started to gain its interest recently because of availability in water treatment for high salt concentration. Especially, integrated MD with RO hybrid process for water desalination show the possibility to treat a high concentration of RO brine for enhancing the efficiency and water recovery. For the successful performance of MD, development of hydrophobic porous membrane should be investigated in future.

In this study, PVC was chosen for the main polymer materials because commercial hydrophobic polymers are still relatively expensive in spite of the decreasing trend of membrane costs. The PVC, then, chloride on the PVC backbones were replaced with hydrophobic monomers via atomic transfer radical polymerization (ATRP) method to improve the hydrophobic characteristics for MD. The grafted PVC-g-octene polymers showed higher contact angle (114 °) and tensile strength than PVC (82 °). The grafted PVC-g-octene polymers were fabricated with both methods thermally induced phase separation (TIPS) and non-solvent phase separation (NIPS) as hollow fiber membranes with changing the concentration of dope solution, additives and bore solutions. The fabricated membranes were applied in the direct contact membrane distillation (DCMD) with various conditions for its performance stability without wetting phenomenon. These membranes exhibited pure water flux with 7.8Kg/㎡·h and high salt rejection with 99.99%. Form this result, the grafted PVC-g-octene porous hydrophobic hollow fiber membranes gave promising potential in DCMD for water desalination.

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Ⅰ. Introduction

1.1. Research background

As an alternative water purification, membrane separation technology has become possible solution for the purpose of producing drinking water due to its high efficiency and low cost. Since the rapid growth of membrane science have brought the reality to apply various lines in industrial wastewater reuse and desalination for providing water (A Razmjou, 2012). Among the invented technologies, reverse osmosis (RO) is the most commonly used for the purpose of seawater desalination (KW Lawson, 1997; MS El-Bourawi, 2006). As a promising desalination by RO, however, has its disadvantages such as low water recovery with generated high concentrated brines. Moreover it requires high pressure that consumes higher energy (B Peñate, 2012).

Membrane distillation (MD) is an emerging membrane separation process that is of thermally driven vapor transport through the porous hydrophobic membranes (Mark A. Shannon, 2008). Since the MD technology was invented by Bodell in 1963, it has started to gain its interest 1990s. The membranes play a role to contain the non-volatile solutes in the feed side completely so that useful various applications such as high boron rejection and process to concentrate solution.

In general, MD process has advantages compared to other membrane separation process that doesn't need a high pressure so that hollow fibers could be suitable for the MD separation process due to their high surface area to volume ratio (AM Alklaibi, 2005). Furthermore, MD can be performed at low temperature of feed solution compared to conventional distillation process and potential applications in wastewater treatment such as removal of hazardous materials, highly concentrated wastewater treatment, and concentration of biological solutions due to its high rejection rate to purify water (above 99.99% of non-volatile components)

The problem of MD is the membrane pore wetting that become a huge obstacle that significantly deteriorate the MD performance that main causes not yet to be implemented commercially. To overcome this, hydrophobic characteristics of membrane must be come first for MD process. In other words, the hydrophobic materials become crucial role of the membrane fabrication for the MD process for maintaining a stable performance in long-term usage commercially. Many researches have been performed for MD process with porous hydrophobic membranes that are commonly employed as commercial membranes such as polypropylene (PP), polyethylene (PE), polytetrafluoroethylene (PTFE), or polyvinylidene fluoride (PVDF) in hollow fibers or flat sheet forms. Feng et al, prepared flat sheet membrane by adopting the hydrophobic materials such as poly (vinyliden fluoride-cotetrafluoroethylene) (PVDF-co-TFE) and poly (vinylidene fluoride-co-hexafluoro propylene) (PVDF-co-HFP). To enhance the hydrophobicity of the membrane, Teoh and Chung used Hydrophobic PVDF–PTFE hollow fiber membrane for DCMD performance study (C Feng, 2004; CS Feng, 2006).

However, the membrane wettability have not yet solved from this commercially used intrinsic hydrophobic membranes.

In order to provide long term stability and better fouling resistance, modification of PVDF membrane has been investigated. So, one of the renowned ways to improve the hydrophobic effect is to reduce the surface energy. Particularly generation of super-hydrophobic materials such as fluorosilanes have become the most widely used for reducing the wetting and fouling explained by Zhang at al. (X Zhang, 2008). From Amir Razmjoualso proposed that superhydrophobic membrane generated by TiO_2 coated membrane with fluorosilanine to improve the hydrophobicity (A Razmjou, 2012). Plasma modification on the membrane surface in order to improve the DCMD performance have been carried out from Li and Wei (CL Lai, 2011; X Wei, 2012). The main advantages for this technique is not only simple one step process, but also hydrophobic materials could be deposited on the membrane surface without functional group to modify the membrane. This unique technique, however, is not easy to control the polymerization on modifying the surface of the membrane. Ceramic membranes were tried to graft with hydrophobic materials for enhancing the high chemical resistance and thermal stability (AE Pagana, 2008; SR Krajewski, 2006). The process of the grafting reaction takes place between hydroxyl groups on the ceramic membrane and hydrophobic organosilane as a hydrophobic chemicals that mostly induced to decrease the pore size of the membrane with a result to reduce the permeate flux. From Fugii at all were reported that hydrophobic silicone were coated on the PVDF hollow fiber membrane to prevent from membrane pore wetting (Y Fujii, 1992). The dried spun hollow fibers were treated with methanol and then the silicon solution was coated after methanol was completely removed. The silicon coated hydrophobic membranes were used for treatment of organic compound in DCMD, but end up decreased the permeate flux compared to the virgin membrane. For maintaining the porosity and pore size after the modification of the membranes, surface modifying macromolecule (SMM) method was proposed for desalination of DCMD by Khayet and Matsuura (Khayet, 2004; J. M. M Khayet, T Matsuura, 2005; T. M. M Khayet, JI Mengual, 2005). This is a new type of membrane modification technique to obtain the higher hydrophobic membrane that synthesized hydrophobic SMM was mixed in the casting solution and the membranes was prepared via phase inversion separation.

It is interesting to mention that the macrovoide free in hollow fiber membrane generally desirable due to their strong mechanical strength and less wetting possibility in membrane distillation in order to maintain the long-term use of the membrane. Therefore, sponge-like structure membranes are prefer for performance in membrane application. For fabrication of highly porous macrovoid free membrane were investigated as lab scale by Bonyadi and Chung that investigate to increase the permeate flux as well as the membrane pore wetting resistance (S Bonyadi, 2009).

Atom transfer radical polymerization (ATRP) is popular as surface-initiated polymerization method that developed for controlled radical polymers. The benefits for this technology is able to control the

polymers structures and utilize various vinyl monomers to develop in many different application purpose. In ATRP, alkyl halogen compounds such as bromides and chlorides are mostly adopted for stabilizing substituents as an initiator of polymer chain backbone as a stable chain growth polymerization. PVC was synthesized as main chains with poly (oxyethylene methacrylate) (POEM) as side chains via ATRP to optimize for CO2 gas separation type of membranes (SH Ahn, 2009).

The purpose for the study is to develop the porous hydrophobic hollow fiber membrane by using PVC after grafted with hydrophobic monomers via ATRP, and investigate its morphology to increase the DCMD performance: even pore size distribution and high porosity in the membrane. To approach this, the application of solvent dope solution two phase flow in the air-gab and addition of the additives (PEG) were further investigated to optimize in order to generate highly porous hollow fiber membranes. To the knowledge of the authors, PVC modification via ATRP method is the first approach for DCMD membrane performance. The fabricated hollow fiber membranes were characterized with morphology, pore size distribution, mean pore size, liquid entrance vacuum pressure (LEVP), and porosity for the DCMD performance test.

1.2. Research objectives

In order to achieve the best permeate flux and enhancing the resistance for the membrane wetting, during the membrane distillation process, asymmetric porous hydrophobic hollow fiber membrane aims to investigate. Hydrophobicity is one of the main factors must be considered for the long term operation in MD. Therefore, we studied three sections for the DCMD performance of hollow fiber membranes with PVC grafted with 1-octene subjected to aqueous feeds at temperature in the range of 50 to 80,

Firstly, the appropriate polymer as poly (vinyl chloride) (PVC) was selected due to its low cost and excellent mechanical strength and chemical properties. The membrane modification were essential for use of MD process by enhancing the hydrophobicity of PVC. Therefore, PVC polymers were grafted with hydrophobic monomers via atom transfer radical polymerization (ATRP). Secondly, the grafted PVC-g-octene, then, investigated to optimize the spinning condition to obtain a symmetric hollow fiber membrane. Lastly, these modified via ATRP asymmetric hollow fiber membranes were tested for desalination by DCMD

1.2.1. For enhancing the hydrophobicity of the polymers via atom transfer radical polymerization to prevent wetting phenomenon in DCMD

Poly vinyl chloride (PVC) is one of the most widely used commercial polymer due to its low cost, chemical stability and mechanical flexibility. Fig. 1 shows comparison of the polymer cost that commercially used for hydrophobic membranes. Atom transfer radical polymerization (ATRP) method makes it possible to attach specific tailored functionalities to the PVC main chains. Thus, modification of PVC by ATRP technique can be a very powerful method. The procedure for ATRP reaction is simple since catalysts and monomers are added to a solvent. The chloride (Cl) groups of PVC begins to react with catalysts that are composed of a transition metal Cu with ligand. The PVC radical started to react with active radical monomers having hydrophobic characteristics. After that, the remaining two radical end-groups combine to terminate the reaction. As a result of the grafting reaction, the PVC polymer can possess hydrophobic surface properties.

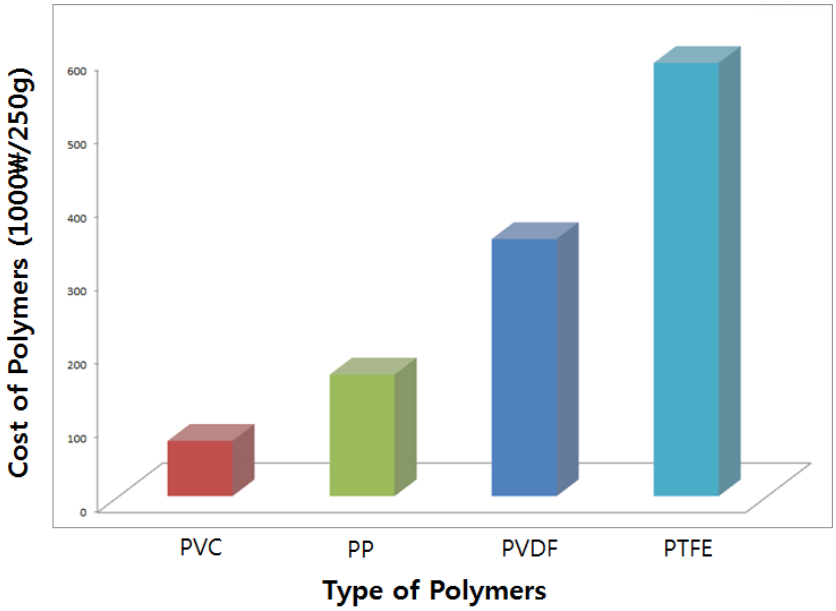


Figure 1. Comparison of the cost in different polymers (PVC, PVDF, PP, and PTFE) from sigma Aldrich.

1.2.2. Fabrication of hollow fiber membrane

For this object, wet-jet spinning process were applied to fabricate symmetric hollow fiber membrane for microfiltration (MF) for application of direct contact membrane distillation (DCMD). The synthesized PVC-g-octene polymers were used as a polymer and polyethylene glycols (PEG-2000) for the effect of the pore formers were added to investigate membrane porosity, mean pore size, membrane mechanical strength and membrane performance test.

1.2.3. Direct contact membrane distillation (DCMD) for desalination

The object in this study were carried out to investigate the possibility for desalination of sea water by applied with synthesized hollow fiber membrane (ATRP). The fabricated hollow fiber membrane were tested in DCMD. The feed and permeate solutions are pumped into the hydrophobic membranes. The hydrophobic nature of the membranes are only allow the vaporized gas penetrate through the membrane, not the feed aqueous solution.

1.3. Concept of membrane distillation (MD)

1.3.1. History of Membrane Distillation (MD)

As an emerging membrane separation process, membrane distillation technology has been developing since 1967 from Bodell based on thermally driven vapor across the porous hydrophobic membranes. Due to the vapor pressure difference, the heat and mass transfer is able to pass through the two side of the membrane.

Bodell first registered Membrane distillation (MD) in US patent on 3 June 1963 and four years later it developed by Weyl Sector and Sasakura Kiai. The first MD paper was published by Findley using DCMD system with various materials in order to meet the membrane hydrophobicity. The second paper published by Findley is mainly focused on major factors influencing heat and mass transfer of water vapor through porous membrane. MD process had been losing its interest quickly due to its lower production of water compared to reverse osmosis (RO) process after a certain period of time, however, MD has regained from a looging brilliant position of academic societies in early 1980s when advent of new membranes with better performance characteristics and application of module. The german company Enka AG published a polypropylene (PP) hollow fiber membrane in tubular modules at the europe-japan Joint Congres on membrane and membrane processes, held at Stresa (Italy) in 1984. Since then, numerous studies has been carried out more in academic fields such as Journal of membrane science and desalination.

Thermal pervaporation or thermo pervaporation was commonly called before the term of Membrane distillation currently use now is decided in workshop on membrane distillation held in ROME (1986). Following that conference, smolders and Franken had integrated related contents of “terminology for membrane distillation” and then united the terms as Membrane distillation. (Fig. 2)

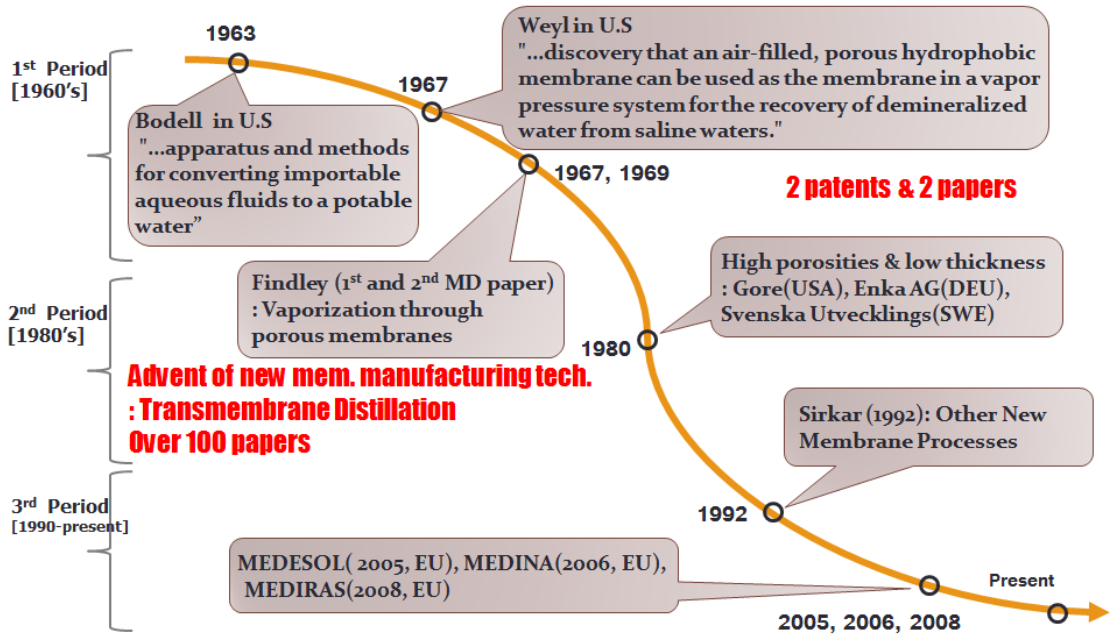


Figure 2. The history of the MD.

1.3.2 Principal of membrane distillation

Membrane distillation (MD) is one of the emerging membrane separation techniques which refers to vapor pressure driven by the temperature differences between feed and permeate solution. After that, thermally driven vapor pass through porous hydrophobic membranes and then condensation occurs at the cool permeate solution.

The porous hydrophobic membranes are not allowed the non-volatile compounds passing through the membranes so that permeate solution is mostly obtained distilled water described in Fig 3.

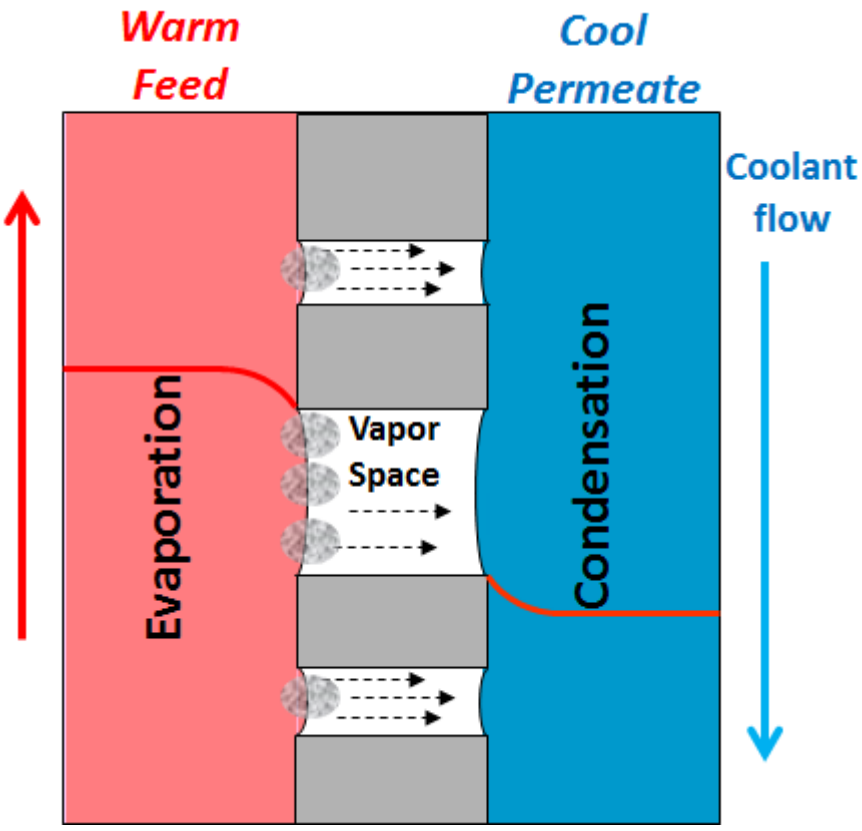


Figure 3. Schematic heat and mass transfer through a single layer hydrophobic membrane in membrane distillation process for the treatment of a feed aqueous solution containing non-volatile solute.

1.3.3. Configuration of MD

A thermally driven process, MD which is water vapor passes through the non-wetted porous hydrophobic membrane. The established driving force is applied to MD technology in order to develop its configurations. There are four process configurations applied in membrane distillation. Each one of the membrane configuration process has its good and bad points for the future potential and vision. The difference of each membrane configuration process in details are shown in Fig. 4

(A) Direct Contact Membrane Distillation (DCMD)

DCMD is the commonly used configuration because of its convenience and simplicity for use compared to other MD process. As mentioned above, temperature differences induce the vaporized pressure that a hot feed solution directly contact a one side of the membrane with a cold permeate solution is circulating another side of the membrane. In this case, the vapor water molecules are able to pass through the porous hydrophobic membrane, but the liquid. Consequently, the vaporized water molecules are condensed in the cold permeate aqua solution. However, DCMD process considers heat lose higher than other configurations due to directly heat transfer through the membranes (S Al-Obaidani, E Curcio, GD Profio, AH Hilal, & Enrico, 2008).

(B) Air Gap Membrane Distillation (AGMD)

AGMD is invented to improve heat efficiency compared to direct contact membrane distillation (DCMD), which is the heat loss by heat exchange conduction by installing a stagnant air gap between the membrane and the condensation surface. The vaporized water molecules are diffused through the stagnant gas gap before the condensation over the cold permeate side of the membrane. As a result, the vapor gas is transferred by natural convection from the temperature difference of the space between air gap and permeate cold side. AGMD, however, has relatively low permeate flux depending on the air gap width (LH Cheng, PC Wu, & Cheni, 2009).

(C) Vacuum Membrane Distillation (VMD)

VMD is designed for increasing membrane permeability by generation of pressure difference between feed and permeate side of the membranes. Therefore, the applied permeate pressure become lower that the vapor gas is being sucked out from the feed side and condensation takes place on the permeate side of the membrane. Advantages of this system are a very low conductive heat loss and increase the permeate flux due to a reduced mass transfer resistance by applied vacuum. However, the complicated technique and higher cost to generate vacuum are required for this method (KW Lawson, 1996; S Bandini, 1997).

(D) Sweeping Gas Membrane Distillation (SGMD)

SGMD consists of a flowing gas, known as air striping, to sweep the vapor out from the permeate side of the membrane instead of permeate solution, thereby condensations of the vapor gas occurs from the permeate side of the membrane in an external condenser. Therefore the problem for SGMD is to keep circulating the cooled walling for the permeate side to maintain the low temperature which increasing its cost. However, compared to AGMD, the higher mass transfer rate is achieved because of its reduction of the barrier for applying driving force (Garcia-Payo, 2002).

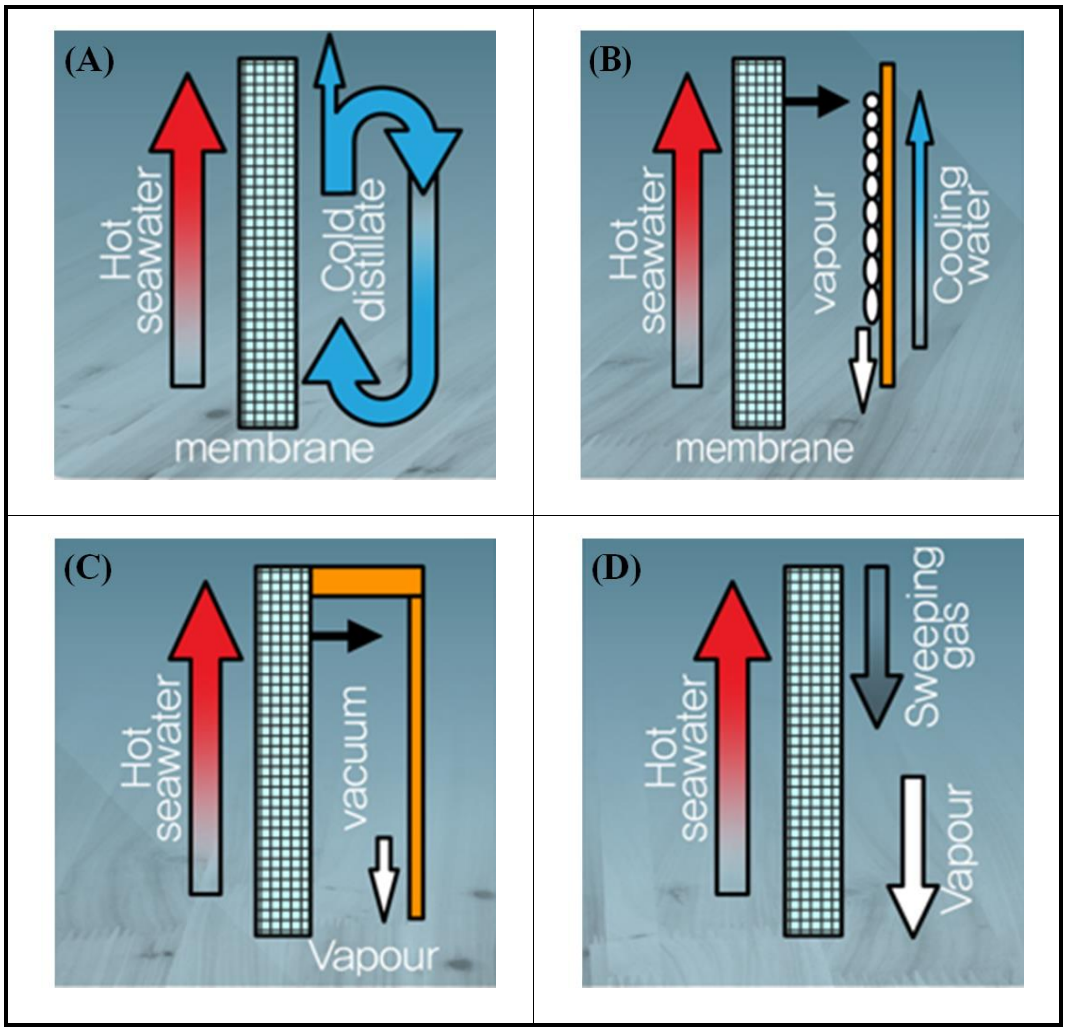


Figure 4. MD process configurations: (a) DCMD, (B) SGMD, (C)VMD, (D)SGMD

Ⅱ. Experimental method and materials

2.1. Materials

In this study, to fabricate low-cost hydrophobic micro filtration membranes, Poly (vinyl chloride) (PVC) was chosen due to its low cost and the good chemical resistance and mechanical properties. Although PVC has many advantages which are able to apply in many different fields, in this work, PVC materials must modify to enhance the hydrophobicity by using Atom transfer radical polymerization and the porosity by adding different amounts of additives.

The hollow fiber membrane were poly (vinyl chloride) (PVC) powder (Mw = 43,000) was obtained from Sigma-Aldrich (USA). For the purpose of contact angle comparison, PVDF-co-CTFE, PVDF-HFP (Mw = 180,000) and PVDF was purchased from 3M (USA), Sigma Aldrich (USA), and BASF (South Korea), respectively. 1-Methyl-2-pyrrolidone (NMP) (99.5%) was purchased from Deajung (South Korea) and used as solvent. Poly (ethylene glycol)-2000 was used for additives as forming pores on the surface of the membrane were purchased from Sigma-Aldrich (USA). CuBr (Ⅰ) and 4, 4′-Dimethyl-2,2′-dipyridyl were supplied by Sigma-Aldrich (USA) as a catalysts for atom transfer radical polymerization (ATRP). For hydrophobic monomer, 1-Octene, was purchased from Sigma-Aldrich (USA). Ethanol (99%) for removal of solvent was purchased from SK chemical (South Korea). Ethylenediaminetetraacetic acid (99%) and Dimethyl sulfoxide (99.9%) for removal of copper salt from ATRP was purchased from Sigma Aldrich (USA) without further purification.

2.2. Preparation of each step of the experiment

2.2.1. Synthesize hydrophobic polymers by using atom transfer radical polymerization (ATRP) method

The synthesis of PVC-g-octene graft method ATRP reactions are described in Fig 5. 45g of PVC was dissolved in 500 ml of NMP in a round bottom flask at 70℃ with electromagnetic stirring for 4 h until it become homogeneous solution. After the solution was cooled to room temperature, 0.1 g of CuBr and 0.5 g of 4,4′-Dimethyl-2,2′-dipyridyl and 81 g of 1-Octene were added to the solution. The solution was purged with nitrogen for 30 min, and then placed in a 70℃ of oil bath for 24 h. After polymerization, it was precipitated in methanol. The grafted resin was added to 10% of EDTA solution to remove copper salt. The polymer was purified by redissolving in DMSO (Dimethyl sulfoxide) and reprecipitating in methanol to purify the solution. The final product as powder was then dried in a heating oven at 50℃ for 48 h.

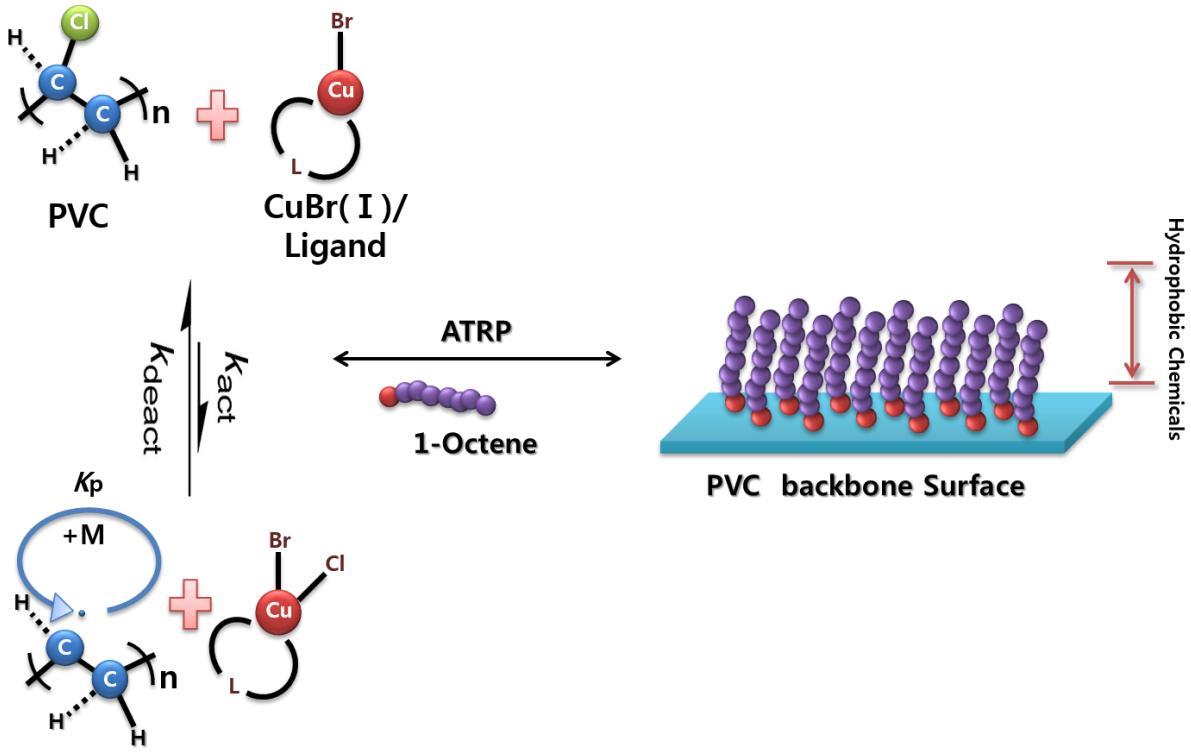


Figure 5. Mechanism of PVC using ATRP

2.2.2. Fabrication of hollow fiber membrane

For the fabrication of hollow fiber membrane, wet-jet spinning process were applied to fabricate hollow fiber membrane for application of membrane distillation (MD) shown in Fig. 6. For enhancing the surface pores and porosity as an appropriate lab scale, dual layer spinneret was applied as the solvent introduced at outer layer of the membrane during the spinning process. The grafted PVC-g-octene polymers were used as a polymer and the effect of the pore formers with the weight of polyethylene glycols (PEG-2000) and its concentration were studied such as porosity, mean pore size, membrane mechanical strength and membrane performance test.

Table 2 and Table 4 illustrate the spinning parameter of the grafted PVC-g-octene to fabricate as the hollow fiber membrane for applying direct contact membrane distillation (DCMD). The PVC-g-octene dope solution were prepared as dope solution and loaded into the spinning dope vessels after degasing process (Table. 2). The dope solution under nitrogen gas pressure and bore fluid by means of GC-pump, were fed into each channel of the spinneret separately at the same time. The bore fluid and outer channel solvent (NMP/H_2O, 8/2) were passed through the central and outer channel of the spinneret each. The dope solutions were extruded from the spinneret and entered into the coagulation bath after exposed at 3 cm of air gab. Tap water was used as non-solvent in the coagulation bath at 20℃ for solidification of hollow fiber membranes. After spinning, the spun fibers were immersed into the water for 3 days for complete removal of residual solvents in the spun fibers. The hollow fiber membrane were then post-treated with glycerin to minimize fiber shrinkage and pore collapse before drying at room temperature. Lastly, the hollow fiber membranes were dried in air over 2 days.

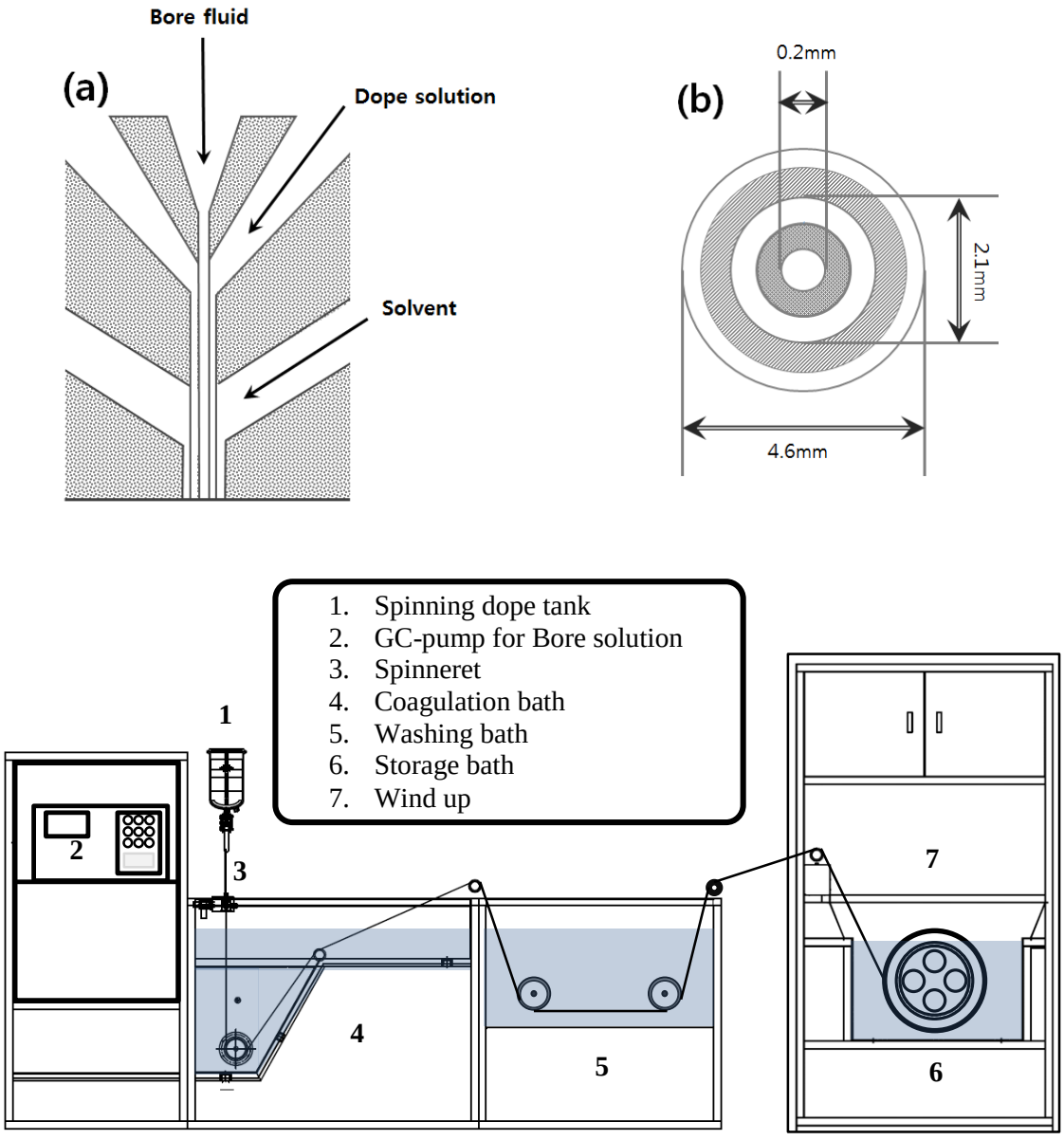


Figure 6. The schematic of dry-wet jet spinning process; (a) Dural-layer spinneret (B) Spinneret size.

2.2.3. Membrane characteristics

2.2.3.1. Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) were employed to observe the prepared membrane morphology (S-4800, Hitachi) at UNIST central research facilities, UNIST, South Korea. In order to observe clear images of the cross-section, the dried hollow fiber membranes were immersed into the liquid nitrogen for fracturing. For observation of Inner and outer surface of the membrane, the fibers were cut into half and positioned on the SEM holder with the fractured hollow fibers. After that the fibers were coated with a platinum layer using a sputter coating to take the SEM morphologies.

2.2.3.2. Water contact angle

The surface contact angles were measured by a sessile drop method equipped with CCD camera (VCA, Billerica, MA). Deionized water ($2\mu\ell$) was dropped on the membrane surface from a needle on a micro syringe during the test. A picture of the drop was captured immediately after the drop set onto the membrane. The contact angles could be calculated by the software through analyzing the shape of the drop. The contact angle θ was an average of 10 measurements.

2.2.3.3. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

The surface chemistry of the pristine PVC and modified PVC hollow fiber membranes and 1-Octene were examined by ATR-FTIR using a Nicolet 6700 spectrometer (Thermo Scientific, USA) with a flat plate germanium (GE) crystal attachment. For obtaining of the spectra, OMINIC 8.1 software was applied to measure the sample. Approximately 64 scans were achieved the signal-to-noise and generated the wave numbers at 600-4000cm^{-1}. The spectral resolution was 4 cm^{-1}.

2.2.3.4. X-ray photoelectron spectra (XPS)

X-ray photoelectron spectra (XPS) were measured using a (Thermo Fisher, UK) system with a K-Alpha (1486.6eV) and a double-focusing hemispherical analyzer in order to identify the major chemical elements. The spot area is approximately 400 um for each sample and the pass energy is 50eV with the binding energy step size of 0.1eV for the acquisition spectra C1s, Cl1s, and Cl2p regions under the vacuum approximately 5×10^{-9}mbar. The high resolution was obtained with binding energy ranges 0.1eV for analyzing the specific.

2.2.3.5. Viscosity measurement

The viscosity of the casting solution was measured by a viscometer (RVDF-Ⅱ, BROOKFIELD, USA). For an appropriate viscosity measurements, select the CP41 spindle and speed setting (10%) and the spindle were immersed into the dope solution at 60℃ to record the viscosity.

2.2.3.6. Measurement of Mechanical property

The tensile strength as one of the mechanical properties was measure by a Universal Testing Instruments (Model AGS - 100 NX Shimadzu). 100 mm length of each fibers were set as starting gauge with 10mm min^{-1} constant elongation rate. At least 10 fibers were tested for ensuring each experiment.

2.2.3.7. Pore size and pore size distribution

To measure the membrane porosity and pore size distribution, the 1100 capillary flow porometer (Porous Media Inc., Ithaca, NY) was employed for the fabricated fibers. A fully wetted sample is placed in the sample chamber and the chamber is completely sealed by epoxy resin. Then, nitrogen gas is allowed to flow into the chamber behind the sample. When the pressure reaches a point that can overcome the capillary action of the fluid within the pore (largest pore), the bubble point has been found. After determination of the bubble point, the pressure is increased and the flow is measured until all pores are empty, and the sample is considered dry. From data plotted in these two curves, the pore size and distribution were calculated by the software from Porous Media Inc. (Ithaca, NY) using the following equation (H Rabiee, 2014).

2.2.3.8. Porosity measurements

The 2 cm long hollow fiber membrane firstly cut into half vertically and weighed after the sample was immersed in pure water for 72 h and wiped by tissue quickly. Then the samples were dried under vacuum oven above 70℃ until a constant weight in a dry state was achieved. The density of the hollow fiber membranes could be calculated using Eq. (1):

$$\overline{\rho} = \frac{m_{dry}}{\left(\frac{\pi}{4}\right)(D^2-d^2)l} \quad (1)$$

where $\bar{\rho}$ was defined as the density of the hollow fibers (gm^{-3}), dry was the weight of the dry hollow fiber samples (g), D was the outer diameter (m), d was the inner diameter (m), and l was the effective length of the samples (m). The membrane porosity ε (%) was defined as the volume of the pores divided by the total volume of the porous membrane. It could usually be determined by gravimetric method, based on the weight of liquid water contained in the membrane pores, as shown in Eq. (2)

$$\varepsilon = \frac{\Delta m}{V \cdot \rho_{H_2O}} \times 100\% = \frac{m_{wet}-m_{dry}}{\left(\frac{\pi}{4}\right)(D^2-d^2)l\rho_{H_2O}} \times 100\% \quad (2)$$

Where m_{wet} was the weight of the wet hollow fiber membrane (g), ρ was the water density (1.0 g cm^{-3}), while m_{dry}, D, d and l were the same as in Eq. (1) (S Atchariyawut, 2006).

2.2.3.9. Measuring Liquid Entrance Vacuum Pressure (LEVP)

LEVP is to detect the vacuum pressure at the breaking point of the membrane from NaCl solution that can be estimated of the membrane wetting. Fig. 7 illustrates that 3.5 wt% NaCl solution in an Erlenmeyer flask was placed in water bath at 25℃. A hollow fiber module including 5 number of fiber samples (20cm length/fiber) prepared by sealing one end of the fiber with epoxy whereas leaving the other end open was connected to the flask. Outside surface of the hollow fiber was exposed to the feed solution, and lumen side of the hollow fibers was connected to a vacuum pump. The feed solution was circulated along the outside surface of the hollow fibers. The salt solution temperature was maintained at 25℃ during the operation. Once the desired set temperature (25℃) of the feed solution was reached, 950mbar of vacuum was applied for 10 min while the conductivity in a round flask filled with distilled water was monitored by a connected computer. After 10 min operation, the vacuum pressure was set 50 mbar lower than the previous one, and the vacuum was applied again for another 10 min. This process kept continued until the conductivity value in the round flask changed sharply. The vacuum pressure at the salt solution penetrated through the membrane was determined as a value of LEVP.

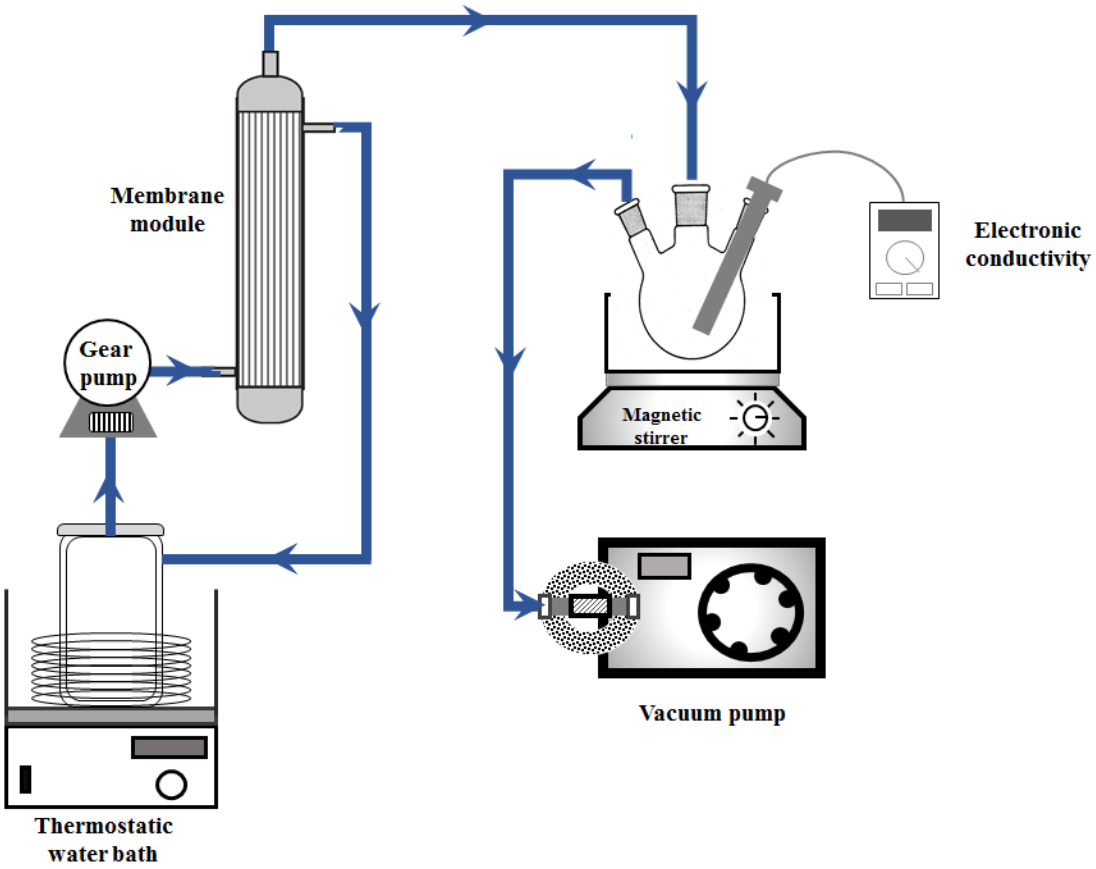


Figure 7. Schematic set up for LEVP.

2.3.10. Membrane performance in a direct contact membrane distillation (DCMD)

DCMD experiments were carried out in continuously as a shown the Fig. 8. The dried PVC-g-octene hollow fibers in number of 15 with 20 cm of effective membrane length were assembled into an acryl tube and were completely sealed by epoxy in each end side for the membrane module. The effective area of the hollow fiber membrane module was 0.01765 ㎡.

The preheated feed solution flowed through the lumen side of the membrane module whereas the cool permeate DI water pumped through the cooling coils flowed through the shell side of the membrane module by gear pump. In order to obtain the desired value, the temperature of feed and permeate side of the solution were continually monitored and controlled by water bath and chiller. The volume of permeate side was measured with electronic balance and the concentration of NaCl in the permeate side was also determined during the 1h tests using a calibrated conductivity electrode (856 Conductivity module, Metrohm, USA) that connected to the computer. The values of the permeate flux were calculated from the equation:

$$J_i = \frac{\Delta V_D}{A \Delta t_i} \tag{3}$$

Where A is effective area and $\triangle V_D$ is the permeate volume collected over a period of time $\triangle t_i$ (h) of the MD process. To measure the solute rejection, 3.5 wt% and 10 wt% of NaCl were used for DCMD performance test. The DCMD rejection R (%) was calculated using the following equation:

$$\mathrm{R}(\%) = 1 - \frac{C_p}{C_f} \times 100 \tag{4}$$

Where C_p is the concentration in the permeate solution and C_f expresses the concentration of the bulk feed solution, respectively.

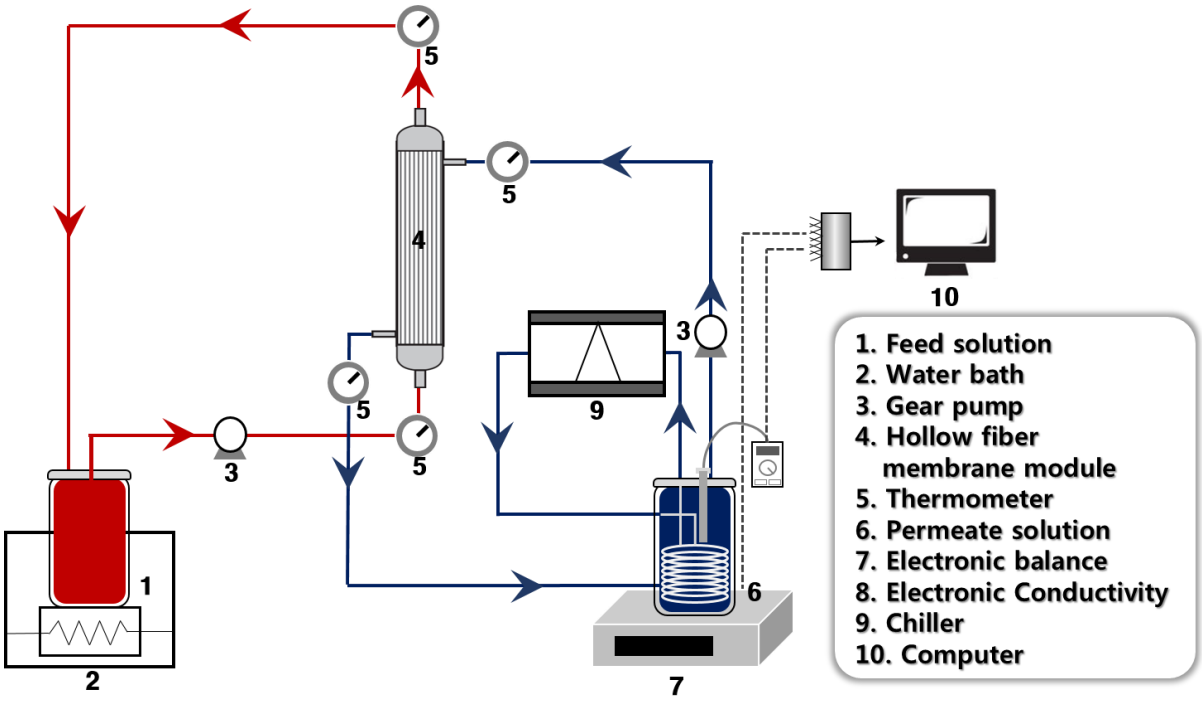


Figure 8. Schematic set up for DCMD

Ⅲ. Results and Discussion

3.1. Evidence of 1-Octene grafted on the PVC polymers

To confirm the successful polymerization of grafted PVC-g-octene, ATR-FTIR were applied due to its easy and efficient way to characterize and identify from the obtained sample. The spectra of pristine PVC, 1-Octene, and PVC-g-octene were examined and shown Fig. 9. The pristine PVC band of C-H stretching mode was slightly observed the intensity at 2863, 2920, and 2966 cm^{-1}. The deformation mode of PVC at 1330 cm^{-1}, and CH_3 stretching mode at 1430 cm^{-1} were also observed respectively. On the other hand, 1-octene of C-H stretching peaks at 2863, 2920, and 2966 $cm^{-1,}$ C-H scissoring peaks at 1465 cm^{-1} can be observed with strong absorbance spectra. For the =C-H stretching mode at 3083 cm^{-1}, C=C stretching mode at 1644 cm^{-1} and C-H methyl rock mode at 1378 cm^{-1} were assigned in 1-Octene additionally. From the results of the spectra between PVC and 1-Octene, the characteristics of the grafted PVC-g-octene peaks can be compared for the successful polymerization. The frequencies in the FTIR spectra of PVC-g-octene was obtained as an increase of C-H stretching peaks at 2863, 2820, and 2966 cm^{-1} which might be influenced by 1-Octene. In addition, C=C stretching mode at 1644 cm^{-1} and C-H methyl rock mode at 1378 cm^{-1} from 1-Octene were completely disappeared so that proved as the results for the reaction between C=C double bond from 1-octene and radicalized PVC. The results of the ATR-FTIR spectroscopy offer the strong evidence that PVC-g-octene is successfully synthesized via ATRP (S Belfer, 2000).

The examination of X-ray photoelectron spectroscopy (XPS) was another way to understand the successful chemical composition in grafted PVC-g-octene hollow fiber membranes. Fig. 10 indicates binding energy and peak areas for C1s and Cl2s and Cl2p for a pristine PVC membrane and modified PVC-g-octene membrane spectra. The binding energy peak at 286.93 eV (C-C, C-H) and at 201.53 eV (Cl) refer to the pristine PVC. For the grafted PVC-g-octene composition demonstrate that the percentage of C elements (284.96 eV) increase as 99.80% while the component of Cl (195.47 eV) become decreases to 0.2%. The increase of percentage of C in PVC-g-octene membrane is due to a result that exchange the chlorides of PVC backbone to the hydrophobic monomers with 1-octene. In other words, 1-octene mostly composed of C that was replaced with Cl on the PVC backbone via ATRP method. Therefore, the total amount of the component in PVC-g-octene in XPS spectra showed the chemical changes that proves the theoretical values to change the intensity of the peak corresponding to Cl decreases almost after grafting by XPS spectra (M Herrero, 2006).

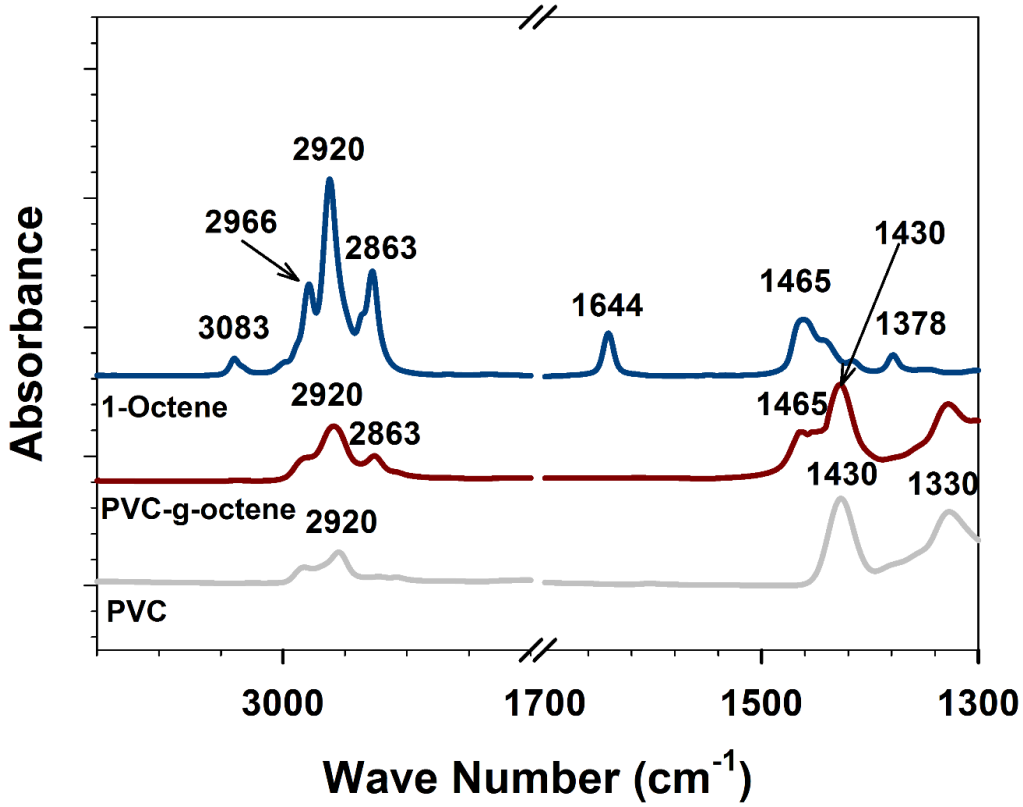
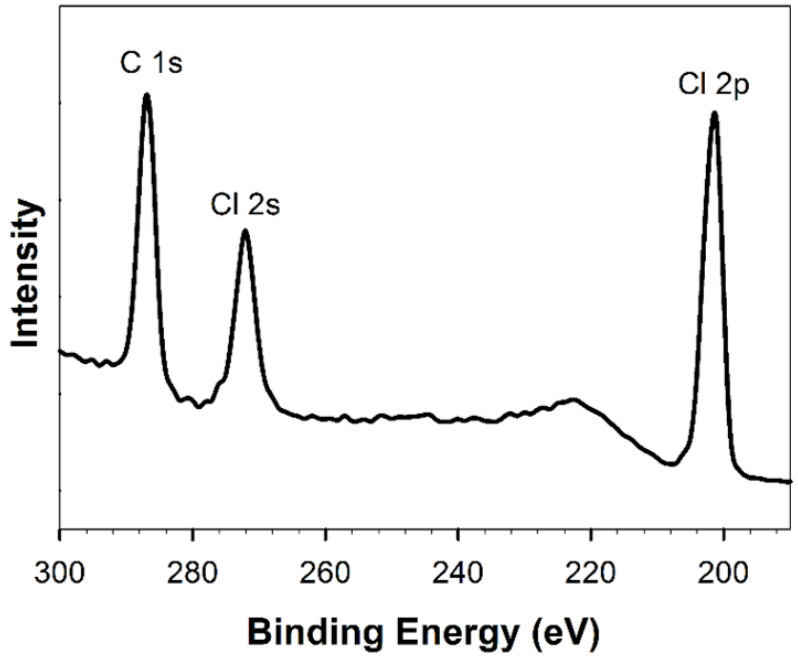
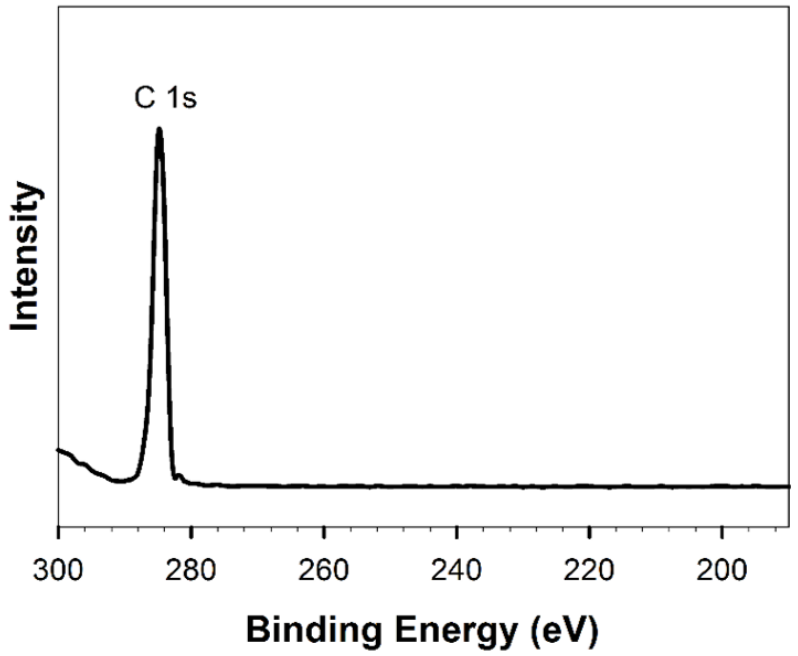


Figure 9. ATR FT-IR spectra of a pristine PVC, PVC-g-octene membrane and 1-octene.





Samples	Composition of grafting PVC (mol%)			
	PVC		PVC-g-octene	
	C-C, C-H	Cl	C-C, C-H	Cl
At. (%)	63.96	36.04	99.80	0.20

Figure 10. Surface characterization of composition of pristine PVC (a) and PVC-g-octene (b) membranes in XPS.

3.2. Hydrophobic properties on the grafted PVC-g-octene membrane

The contact angle measurements are the one of the common methods to determine the hydrophobic nature of the grafted membrane characteristics. The average water contact angles were measured before and after modification of PVC membrane so as to know successful grafting of PVC-g-octene as well as hydrophobic properties. Fig. 11 illustrates the contact angle change of the PVC-g-octene membrane against the pristine PVC membrane. The contact angle of the virgin PVC membrane was 82.9±3.5° and the grafted PVC-g-octene membrane increased 114.5±2.9°, respectively.

Therefore, from comparison of water contact angle between a pristine PVC and the modified PVC-g-octene membrane shows that PVC-g-octene was successfully grafted via atomic transfer radical polymerization (ATRP) with an increase of hydrophobic characteristics that a desired way for membrane distillation (MD).

The fig. 11 suggests the comparison of the contact angle with various type of hydrophobic polymer membranes. The grafted PVC-g-octene shows the highest contact angle among other type of polymer membranes while the receding contact angles were 93.2±2.4, 82.9±3.5, 88.4±2.0, and 102.4±1.9 for the PVDF-HFP, PVC, PVDF, and PVDF-co-CTFE membrane, respectively. This results demonstrate that hydrophobic modification of this membrane found to be a comparable among those hydrophobic polymers

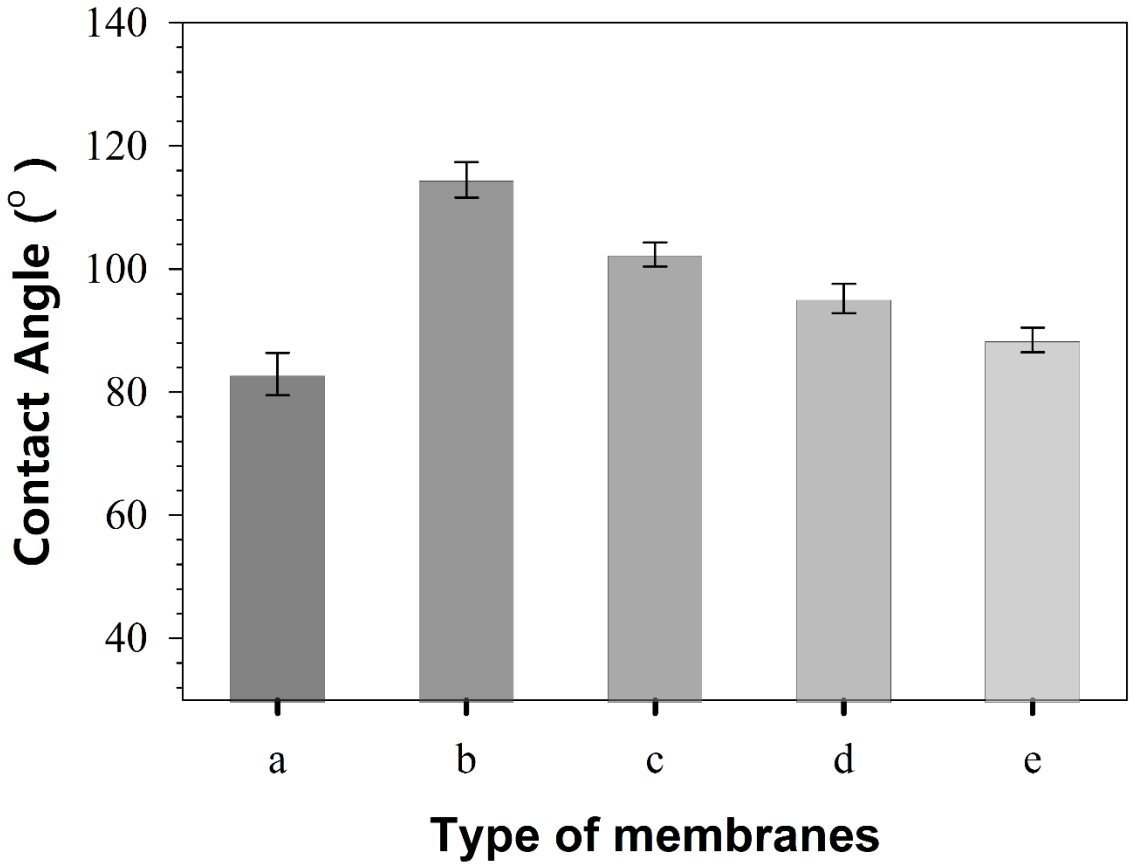


Figure 11. Contact angle comparison (a) PVC, (b) PVC-g-octene, (c) PVDF-co-CTFE, (d) PVDF-HFP, and (e) PVDF membrane

LEVP is another critical membrane characteristics for hydrophobicity of MD was measure. The LEVP was developed to apply as a performance evaluation parameters of the membrane wetting that was designed firstly from our lab. Table 2 indicates that the synthesis for PVC polymers reduce the LEVP values from 700mbar to less than 40mbar which means to improve the resistance from water entrance through the membrane although the pore size and porosity become larger than the PVC hollow fiber membranes. This might be the presence of C-Cl in the PVC increase the surface energy with an increase of reactivity that results to reduce the hydrophobicity of the membrane. Therefore, substituting the chemical component from Cl to 1-Octene in native PVC via ATRP will play the role to reduce the surface energy (AG Karakeçılı, 2002; P Teixeira, 1999).

3.3. Fabrication of hollow fiber membranes

3.3.1. The introduction of TIPS and NIPS methods

Most common methods for fabrication of membranes in phase inversion are thermally induced phase separation (TIPS) and Non-solvent induced phase separation (NIPS). The membrane prepared by phase inversion method has been used commercially due to its advantages of low producing cost and simplicity of manufacturing process. For NIPS method, dissolving the polymer in a solvent to create a homogeneous solution is immersed into a non-solvent that phase transition occurs from liquid to solid. Therefore, pores are formed in the membranes while demixing between solvent and non-solvent takes place. Prepared membranes by NIPS, generally, may have porous asymmetric structures so that the membranes are a relatively low tensile strength. The advantages of this method is easier to control the structure such as pore size and porosity of the membranes compared to TIPS (SS Kim & Lloyd, 1991).

On the other hand, thermally induced phase separation (TIPS) is dependent on heat transfer that the homogeneous solution mixed between polymer and diluent induces phase separation by cooling to remove the heat from the hot solution. Commercially available TIPS membranes are polypropylene (PP), Polyvinylidene fluoride (PVDF), and Polyethylene (PE). The TIPS membranes have relatively high mechanical strength and symmetric morphology with high average pore diameters. The advantages and disadvantages of NIPS and TIPS phase inversion methods are summarized at Table 1.

Table 1. Comparison between TIPS and NIPS

NIPS	TIPS
- Change in composition by the addition of non-solvent. - Exposure to vapor or immersion in non-solvent bath. - Pros : Easy casting method - Cons : The formation of large pores and low tensile strength	-Converting two phase mixture via the removal of thermal energy rather than by the exchange of non-solvent and solvent for immersion precipitation-induced phase inversion membranes - Pros : Easy to adjust the structure, high tensile strength - Cons : Hard to fabricate the membrane by the high temperature

In this study, we have studied both method NIPS and TIPS to fabricate hollow fiber membranes in order to apply to DCMD.

3.3.2. Thermally induced phase separation (TIPS)

PVC-g-octene polymers with γ-Butyrolactone was introduced to fabricate hollow fiber membrane via thermally induced phase separation (TIPS) (B.J. Cha & Yang, 2007). For understanding of the membrane characteristics, the different parameters such as polymer concentration, nuclei agents and water flux were investigated for desalination purpose in direct contact membrane distillation (DCMD). The spinning conditions for PVC-g-octene hollow fiber membranes are below the Table 2.

Table 2. Spinning parameters of PVC-g-octene hollow fiber membranes for TIPS

Parameters	Operating conditions
Extrusion pressure (bar)	2
polymer solution temperature (℃)	80
Bore fluid	GBL
Bore flow rate (ml/min)	6
External coagulant	Tap water
Bore fluid and external coagulation temperature (℃)	20℃
Air gap distance (cm)	3
Take up speed	Free
Post-treatment	Tap water

The hollow fiber membranes produced with different polymer concentration and different additives are shown in Table 3.

Table 3. The condition for hollow fiber membrane

	Type of membrane	LEVP	Porosity	Water Flux (LMH)	Rejection (%)
A	PVC-g-octene/GBL (25/75)	less than 40mbar	57.76	0.95±0.09	99.99
B	PVC-g-octene/GBL/ (30/70)	less than 40mbar	54.64	0.54±0.08	99.99
C	PVC-g-octene/GBL (35/65)	less than 40mbar	51.25	0.21±0.04	99.99
D	PVC-g-octene / PMMA / NMP (25/10/65)	less than 40mbar	58.21	2.27±0.15	99.99
E	PVC-g-octene / PEG-400 / NMP (25/10/65)	less than 40mbar	60.34	2.42±0.23	99.99

3.3.2.1. Effects of polymer concentration

The grafted PVC-g-octene polymers were prepare with thermally induced phase separation (TIPS) for application of DCMD. Fig. 12 shows the SEM images of PVC-g-octene with different conditions. For the cross section images implying that the pore size slightly decreases with an increase of the concentration of PVC-g-octene polymers in dope solution. As the polymer concentration increased, the temperature difference between polymer and diluent crystallization was increased and more structures had more time to change the size. Furthermore, when the polymer concentration increase its concentration results in a number of nuclei that is reduce the pore size as a results (C Chiang & Lloyd, 1996).

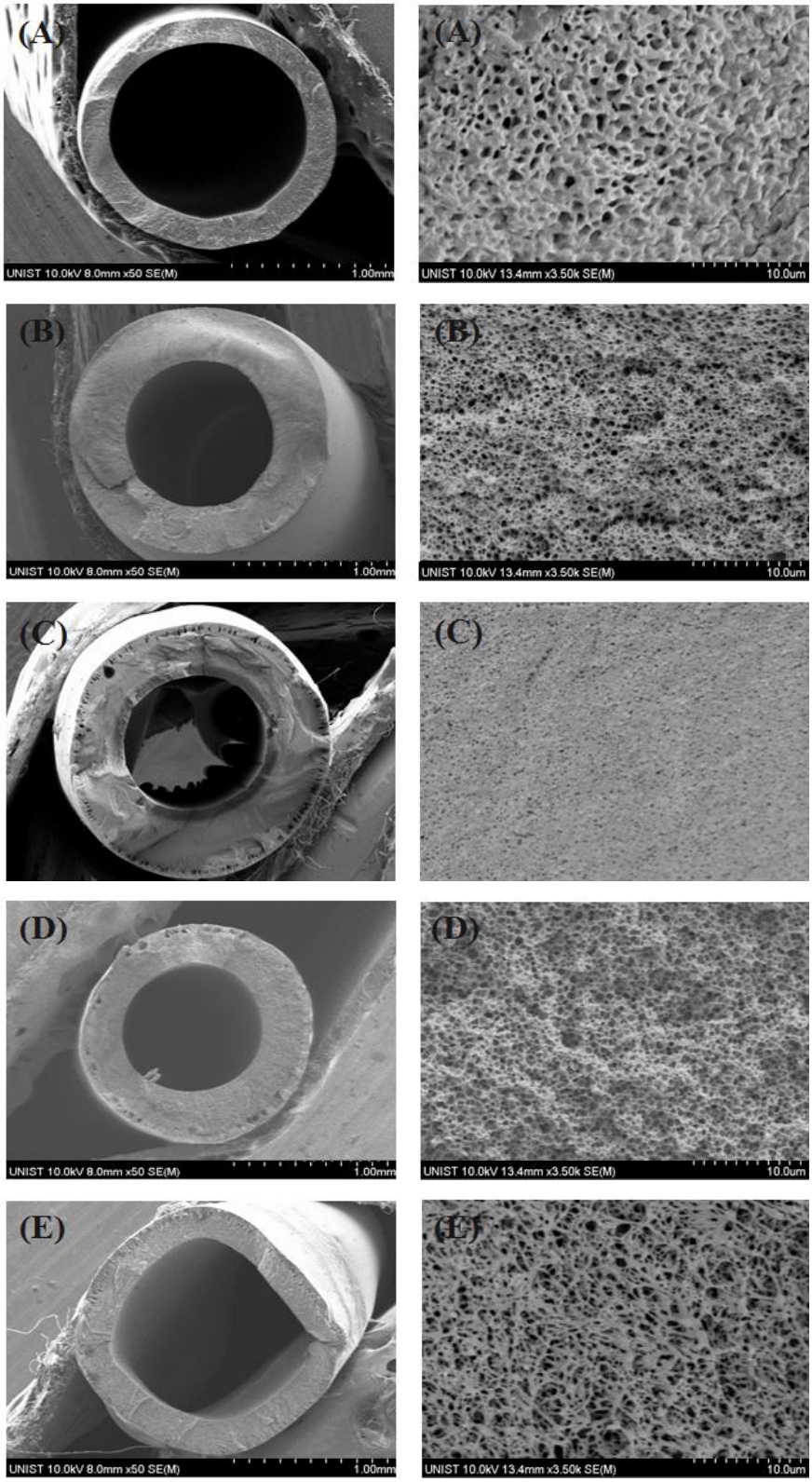


Figure 12. Cross section SEM images of PVC-g-octene with different dope solution fabricated via TIPs.

3.3.2.2. Effect of nucleating Agents

Adding nucleating additives could be one of the ways to control the polymer crystallization kinetics especially the control of membrane final morphology. The addition of nucleating agent accomplishes practically formation of narrow pore size formation and an increase of pore size. In other words, addition of PGE increases the growth of droplets that result in increase of pore size (B Luo, J Zhang, X Wang, & Y Zhou, 2006). In addition, the effects of polyethylene glycol (PEG) on the phase behaviors is partly reducing the cooling rate which shows positive impact on the porosity and water flux of PAN membrane (DR Lloyd & Lim, 1993). From the SEM images shown in Fig. 12 indicates that the addition of PEG in dope solution observed that spherulite size of PVC-g-octene membrane increased that the porosity of PVC-g-octene membranes improved as well. For the surface morphology images according from Fig. 13 shows that nothing much changed before used PEG as used as additives. For E case, the pores appears on inner surface of hollow fiber membranes but not observed on outer surface of the membrane. This is partly the PEG works as pore forming with NMP as bore solution for the delayed the crystallization that affects the membrane structures.

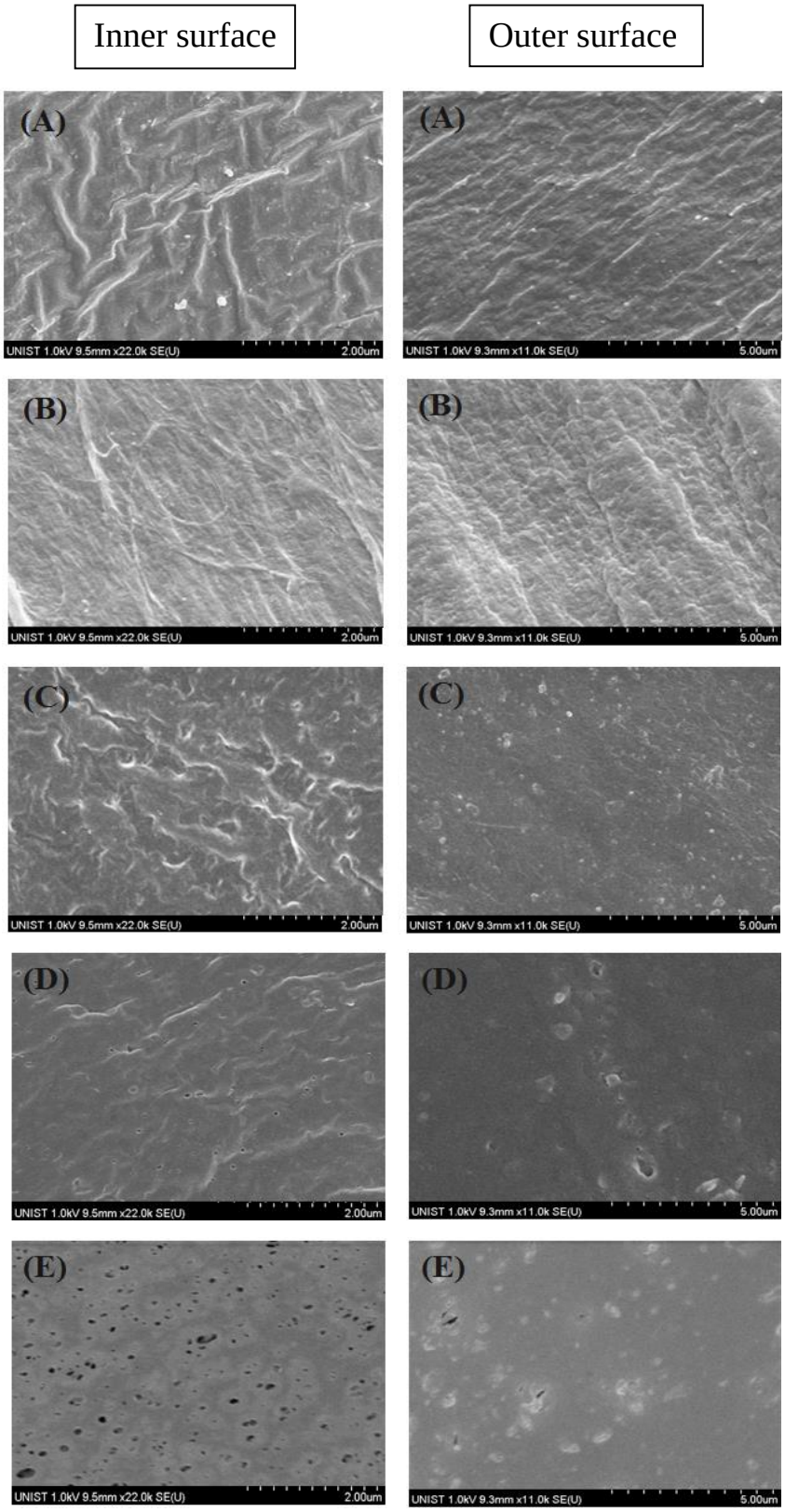


Figure 13. Surface morphology of PVC-g-octene hollow fiber membrane fabricated with different conditions via TIPs.

3.3.2.3. DCMD performance Test

The results of the DCMD performance was shown in Fig. 14. The permeate flux is proportional to the concentration of polymers in dope solution. The porosity is decreased as well as the pore size when the increase of polymer concentration, as we can see from the SEM cross section images.

In the case of applying different types of additives shows that PEG shows the highest permeate water flux. Types of additives affects the kinetically in pore sizes and porosity on the membranes that PEG shows high porosity and pore size than PMMA. Another reason for this is the membrane thickness increase with an increase of polymer concentration. Generally, the permeate flux in MD is inversely proportional to the membrane thickness. This factor will reduce the water vapor pressure through the membrane (N Tang, 2010). Lastly, in order to support for the DCMD data, with PEG, the hollow fiber membrane shows pores on the surface of hollow fiber membrane which is related to the permeate flux in DCMD. In results, F shows the best permeate flux (1.45 $Lm^{-2}h^{-1}$) compared to others due to its high porosity and surface pores in membrane.

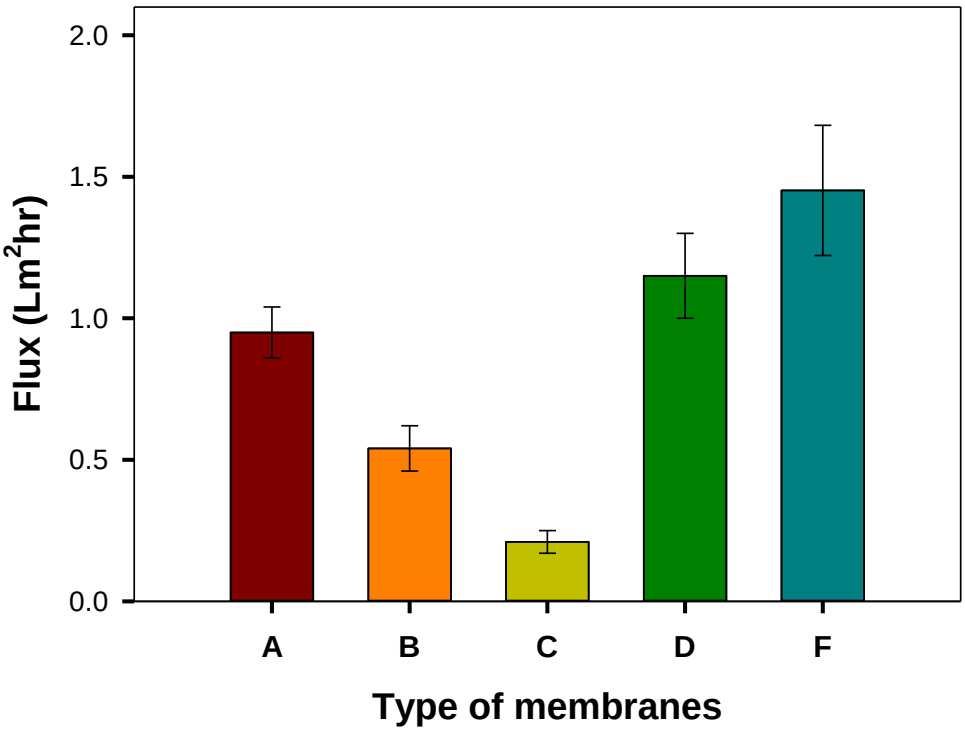


Figure 14. Pure water flux with different conditions of membranes via TIPs.

3.3.3 Non-solvent phase separation (NIPS)

3.3.3.1. Membrane characterization

For the comparison before and after grafted PVC polymers, a pristine PVC and grafted PVC-g-octene membrane with different amount of additives (PEG2000) were prepared as hollow fiber membranes.

Table 4. Spinning parameters of PVC-g-octene hollow fiber membranes for NIPS

Parameters	Operating conditions
Extrusion pressure (bar)	2
polymer solution temperature (℃)	60
Bore fluid	NMP/H_2O (8/2)
Outer channel solvent	NMP/H_2O (8/2)
Bore flow rate (ml/min)	6
External coagulant	Tap water
Bore fluid and external coagulation temperature (℃)	20
Air gap distance (cm)	3
Take up speed	free
Post-treatment	Tap water

Table 5. Composition of the casting solution and its characteristic

Batch (No)	Dope composition			Viscosity	Mean pore size (㎛)	Water flux ($Lm^{-2}h^{-1}$)	LEVP (mbar)
	Polymer (wt%)	Solvent (wt%)	Additives (wt%)				
A	PVC (25)	NMP (75)	0	4560	77.45±1.22	0.84±0.19	700mbar
B	PVC-g-octene (25)	NMP (75)	0	7408	65.40±2.67	0.76±0.12	less than 40mbar
C	PVC-g-octene (25)	NMP (72)	3	12305	55.59±4.59	1.25±0.25	less than 40mbar
D	PVC-g-octene (25)	NMP (69)	6	18732	59.63±2.3	1.98±0.31	less than 40mbar
E	PVC-g-octene (25)	NMP (66)	9	22760	66.33±1.31	2.56±0.32	less than 40mbar
F	PVC-g-octene (25)	NMP (63)	12	45120	69.32±3.94	3.43±0.49	less than 40mbar
G	PVC-g-octene (25)	NMP (60)	15	78450	73.23±3.82	7.92±0.74	less than 40mbar

In order to have better understanding for the effect of grafting and additives on the membrane structures, the cross section and inner and outer surface of the membranes morphologies were observed by scanning electron microscope (SEM). Fig. 15 and 16 shows the SEM images with cross-section and inner and outer surface images of the hollow fiber membranes. The SEM images shows that appeared the different structures among the PVC and grafted PVC-g-octene with different amount of PEG2000 in dope solution as hollow fiber membranes. Generally, a symmetric membrane with macrovoids and dense skin was observed when the casting solution is soaking into the non-solvent (water) directly because it leads the instantaneous demixing. In other words, the fast diffusion rate occurs during the membrane formation (TH Young, 1991a, 1991b). The SEM images from PVC and PVC-g-octene hollow fiber membranes in cross-sectional images correspondently shows both finger-like structure with dense surface morphology. Another interesting point is that the structure of PVC-g-octene hollow fiber membranes appears lesser macrovoids and smaller pore size than PVC this might be due to the higher viscosity which leads the delayed demixing. In the case of PVC-g-octene, the viscosity increase might be the reason for the longer chain of the polymer structures become enhanced the entanglement of the polymers after grafting of pristine PVC polymers.

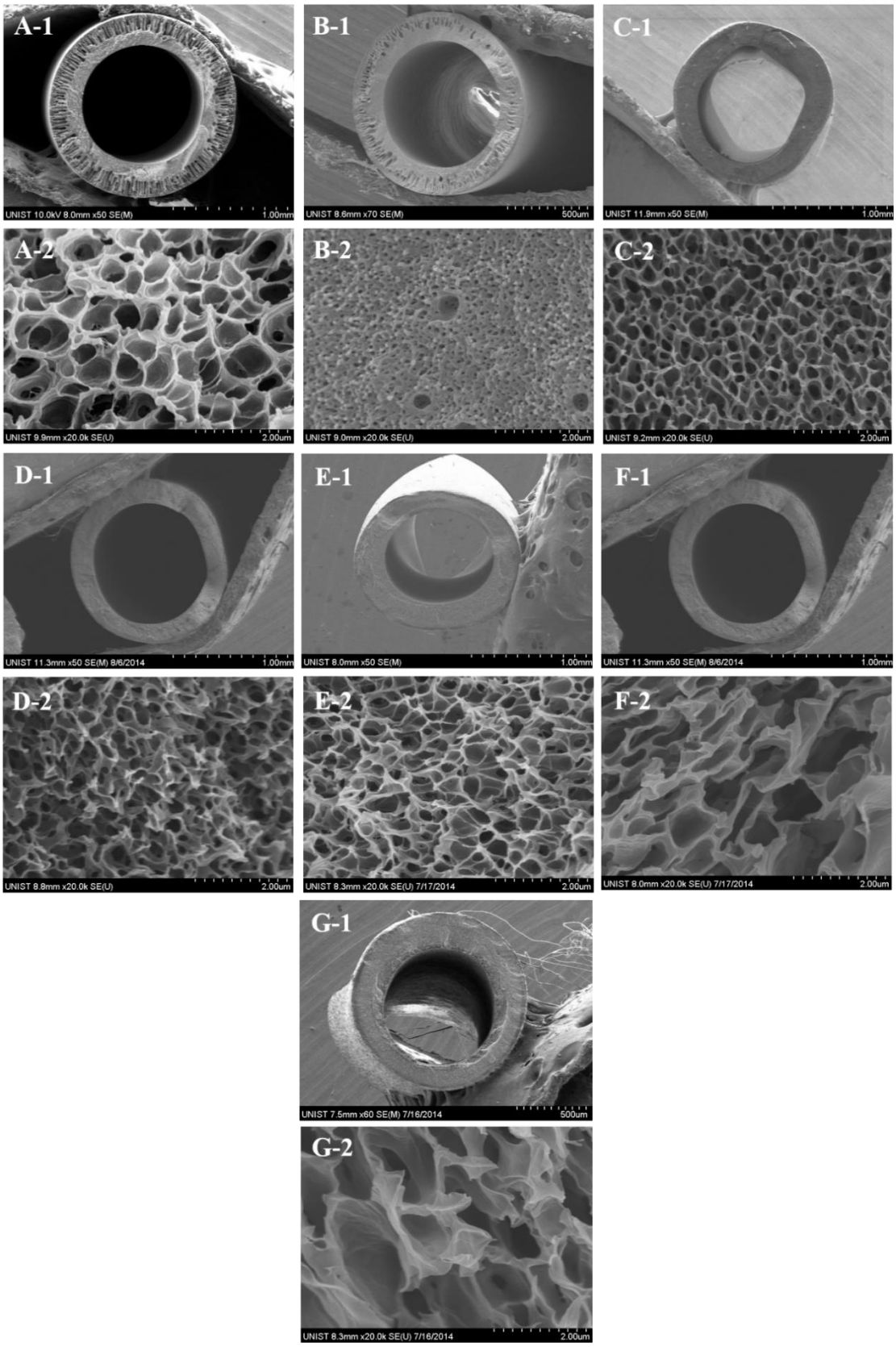


Figure 15. SEM images of cross section of PVC-g-octene with different dope solution concentration via NIPs.

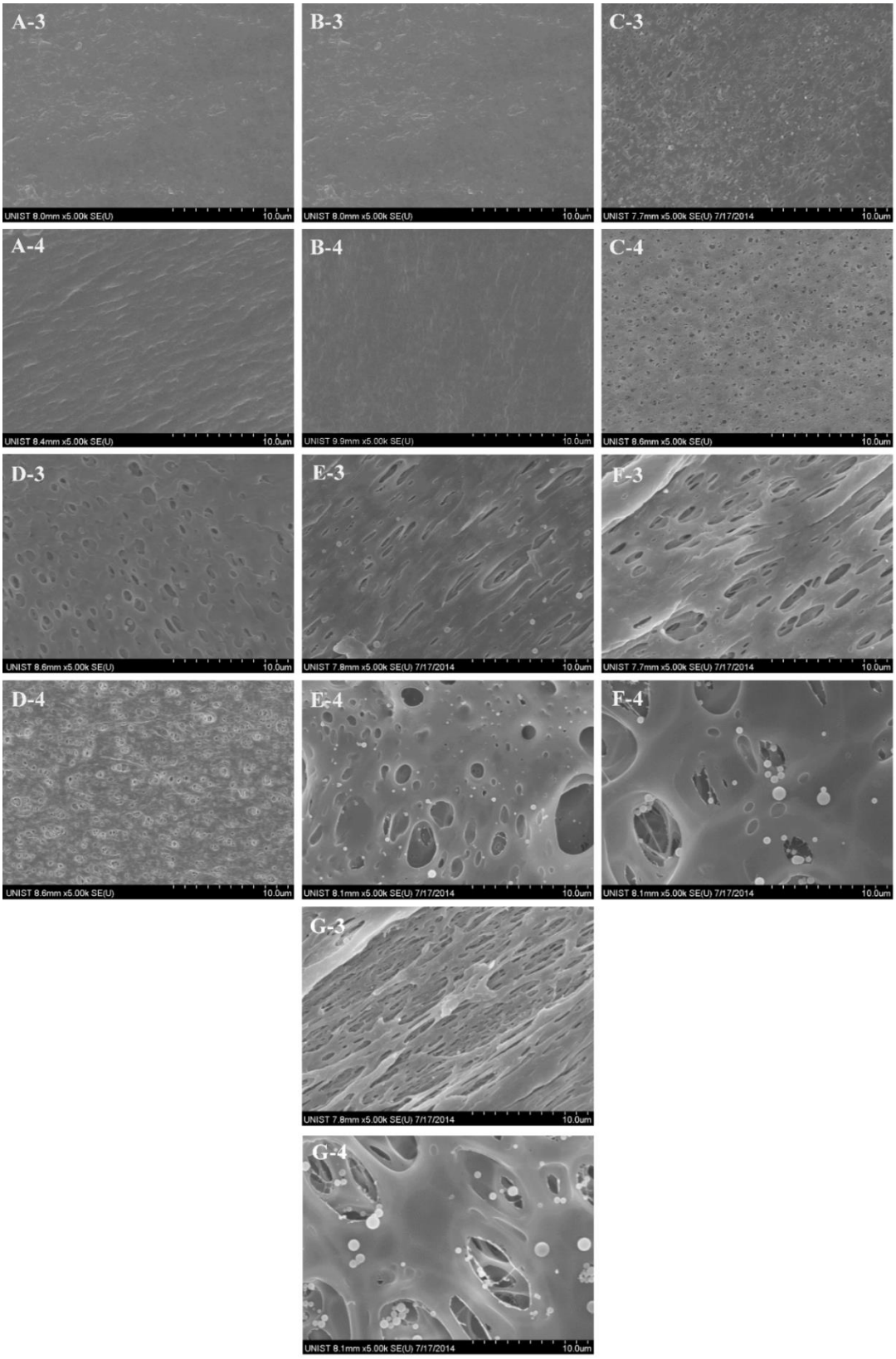


Figure 16. Surface SEM images of PVC-g-octene hollow fiber membrane fabricated with different concentration via NIPs.

Table 5 shows that non-solvent additives in dope solution with PVC-g-octene increase the viscosity. The viscosity of PVC-g-octene without additives was 7408, but it increases while the amount of PEG increases from 3 to 15wt% in dope solution that the viscosity enhanced ranging from 12305 to 78450, respectively. Considering at low viscosity of PVC-g-octene without additives, the cross sectional images in Fig. 15 appeared as finger-like structure. When the viscosity increased with the addition of PEG in dope solution, however, the morphology of the membrane turned into sponge-like structure because it creates the slow solidification process as high viscosity value. This is mainly due to an increase of the viscosity in the modified PVC-g-octene dope solution that induced slow coagulation rate with the increase of the dope solution concentration (H Strathmann, 1977; MA Frommer, 1970). The presence of PEG also play a role to give the effect on the membrane pore size. From the cross section images indicates that when dosage of PEG in dope solution increase, the pore size were found to increase. Another factor for forming the macrovoid free membrane structure is the flowing solvent (NMP/H2O, 8:2) on the outer surface of the spun dope solution that leads a delayed demixing.

At the same time, the surface pore size also were influenced by an increase of the amount of additives. The observed surface morphology from PVC and PVC-g-octene without additive exhibited no pores on inner and outer surface of the membranes. As the PEG additives were added into dope solution, the surface pore started to form (S Bonyadi, 2009). Interestingly, the pore size on the surface membrane become increased as an increase of the amount of the additives. It might make a deduction that PEG works as pore formers during the formation of membranes that results in enlargement of mean pore size (A Idris, 2006; T Hou, 1991). Even though the hydrophilic characteristic PEG in dope solution would lead the thermodynamically less stable that induced the rapid instantaneous demixing during the phase inversion process, the solvent (NMP/H2O, 8/2) flowing on the outer dope solution induce a delayed demixing in that the non-solvent (H_2O) may hinder the intrusion into the solvent. Thus, the pore forming effect of PEG is considerably efficient on the surface morphology that may increase the surface pore size and porosity (A Idris, 2006; T Hou, 1991). However, the exact mechanism has not yet been clear.

Porosity is one of the parameters to decide membrane mass transfer in membrane distillation process. Generally, the effective high porosity determined in producing higher clean water from membrane distillation. Usually, when the membrane polymer concentration in dope solution increases, the porosity decrease which is related to the morphology of the hollow fiber membrane. In other words, the finger like structures mostly have higher porosity value than sponge like structure. From the Fig. 15 and 16 interestingly, when the concentration of PEG in dope solution was increased, a gradual increase of porosity and pore size was observed. For the hollow fiber membranes prepared the concentration of PEG from 3% up to15 % in dope solution, the porosity of PVC-g-octene membrane increase from 52.07 to up to 73.23%. This is because PEG acts as pore forming agents to make a more open structure of the membrane. According to the Figure 17, the larger pore diameters was formed as the PEG2000 increased in the dope solution. The pore diameter of the membranes become overall 0.2um when the 15wt% of PEG used in the dope solution which results in enhancing the DCMD performance test. Therefore, an increase of the concentration of the non-solvent PEG in dope solution increase the porosity with better MD permeability as a result (PST Machado, 1999; T He, 2003).

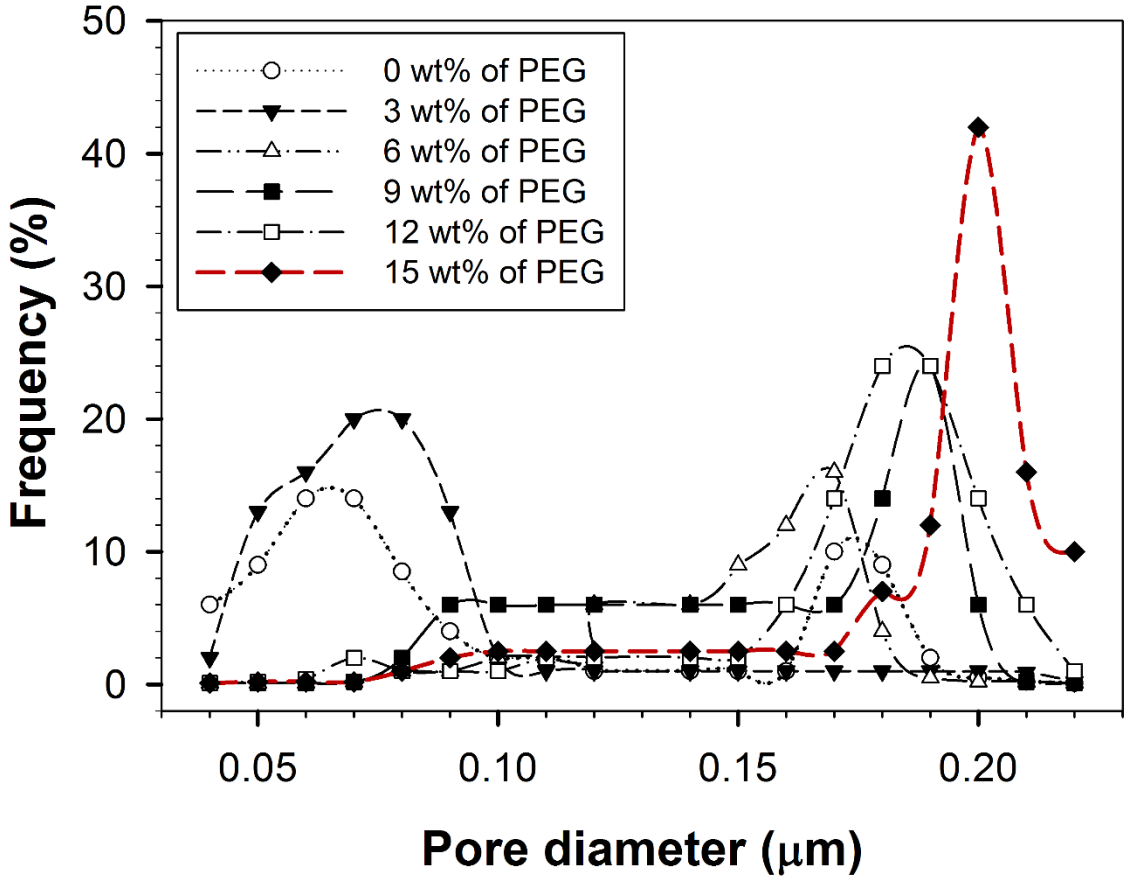


Figure 17. Pore diameter distribution of PVC-g-octene hollow fiber membranes with different concentration of PEG-2000 (a) 0 wt% of PEG (b) 3 wt% of PEG, (c) 6 wt% of PEG, (d) 9 wt% of PEG, (e) 12wt% of PEG (f) 15wt% of PEG

On the other hand, the tensile strength from Fig. 18 described that kept decreasing while the amount of PEG increases. This may be explained as the relationship between tensile strength and porosities in PVC-g-octene hollow fiber membrane with different amount of non-solvent additives showed reverse proportional way. This is because enhancing the concentration of additives in the dope solution enlarge the pore size and porosity on the membrane while the mechanical properties decrease (DJ Lin, 2006). Compared with PVC-g-octene without additives shows higher porosity than PVC-g-octene with3wt% of PEG. As explained in Fig. 15, the cross-sectional SEM images proves that the finger-like structure turned into sponge-like structure which is macrovoid free membranes due to increase of viscosity when the PEG2000 was added into the dope solution.

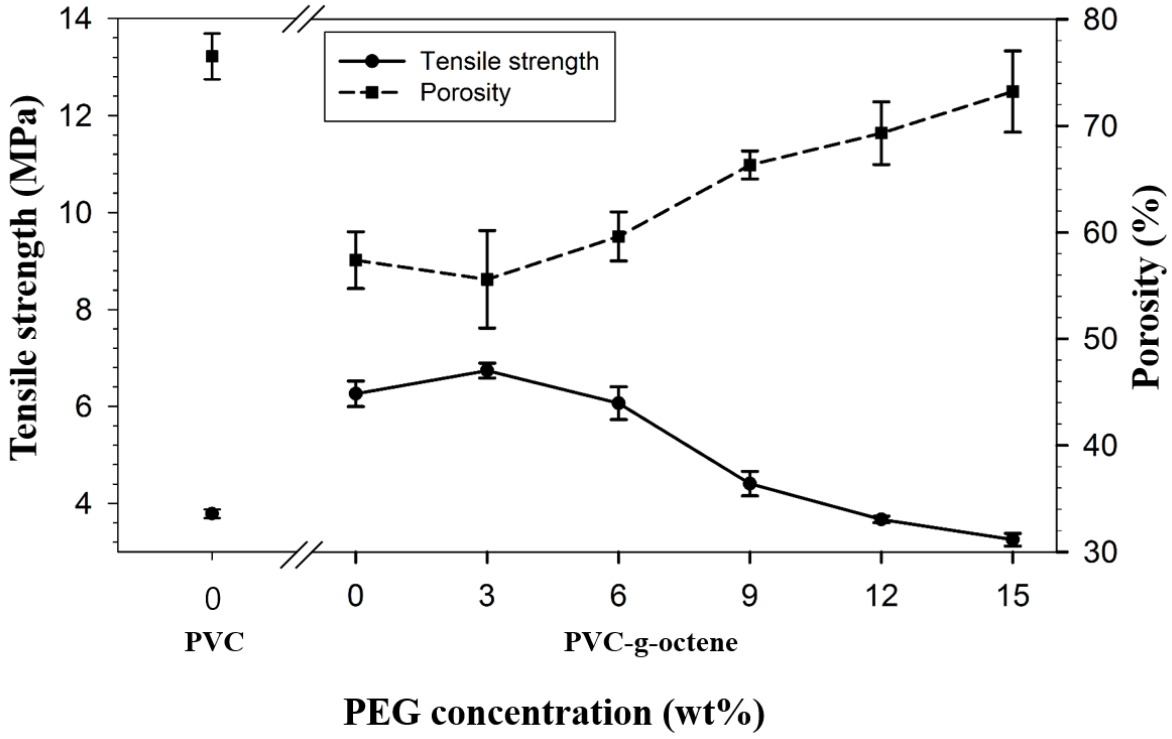


Figure 18. Effect on the concentration of PEG2000 (0, 3, 6, 9, 12, and 15wt %) in PVC-g-octene dope solution and its relationship between tensile strength and porosity of the membrane

3.3.3.2 DCMD performance

In order to see the potential possibility for desalination, the fabricated hydrophobic porous PVC-g-octene hollow fiber membrane was evaluate for DCMD performance test. Based on high porosity and pure water flux hollow fiber G was chosen as main fibers to make a module for the experiment. Various DCMD operating conditions were investigated for grafted PVC-g-octene hollow fiber membrane to understand of membrane capability for DCMD and optimize the best result performance. Therefore, the effect of operating parameters such as concentration of feed solution, feed temperature, feed flow rate, and a long term DCMD performance were studied.

3.3.3.2.1 Effect of various condition of feed temperature in DCMD

Various conditions of fabricated hollow fiber membranes were tested for DCMD performance. Table 5 shows that PVC and PVC-g-octene shows lowest permeability flux at 0.84 and 0.76 $Lm^{-2}h^{-1}$ respectively. This seems mainly because of the low porosity and pore size on the surface of the membranes although the membrane morphology shows many macrovoids with high porosity. The permeate flux based on Table 2 also indicates that the permeate flux kept increasing when the PEG ratio increase from 3 wt% to 15 wt% in the dope solution in that the best performance test was achieved the highest flux at 7.92 $Lm^{-2}h^{-1}$ as well as highest salt rejection above 99.99% at feed and permeate temperature 60 and 20℃, respectively. In order to explain the obtained results, the SEM images of the top layer, and the cross sections from the Fig. 15 and 16 showed that when the concentration of PEG increase in dope solutions, not only the pore size and porosity become lager on the cross section of the membranes, but also increases on the surface membrane. This is because higher PEG concentrations in dope solutions forms bigger pores in the membranes. Additionally, the porosity also increased as the increase of PEG in dope solution. The water permeability in MD is related proportionally to the membrane pore size and porosity that results in a positive effect on the performance of the membranes. The grafted PVC-g-octene hollow fiber membrane was tested for the DCMD performance with different feed temperature. The effect of the feed temperature on the permeate flux applied to ranges 50℃ to 80℃ in the DCMD process. The permeate temperature was kept at 20℃. For the experiments, high salt rejection rate that is 99.99% were obtained from different NaCl feed solutions (NaCl, 3.5, 7, and 10 wt%). Fig 19 indicates that the permeate flux rise up as the temperature increases from 50℃ to 80℃. The permeate flux increase 34.2 $Lm^{-2}h^{-1}$ as the feed temperature increase up to 80℃. This is because the main driving force of DCMD is the water vapor pressure which increases as increasing temperature exponentially. Therefore, the higher temperature may enhance the driving force which leads substantial increase mass transport from hot feed to cold permeate side (A. V. M Khayet, JI Mengual, 2004; C. F.

M Khayet, KC Khulbe, T Matsuura, 2002). For the higher NaCl concentration in the feed solutions (7, 10 wt %), the less permeate flux was observed comparing with 3.5 wt% of NaCl feed solution. This phenomenon is mainly because the increase of the non-volatile solute concentration in the feed solution influence to decrease water vapor pressure. Another reason is the mass transfer coefficient of the feed solution become decreased by the increase of the concentration polarization on the membrane surface which leads to enhance the salt concentration on the membrane surface (E Curcio, 2005).

High concentration of brine water treatment have been still remained as one of the major challenges in RO system. However, DCMD experiment experiments showed the capable of high concentrated brine water treatment as an alternative desalination process (JP Mericq, 2010).

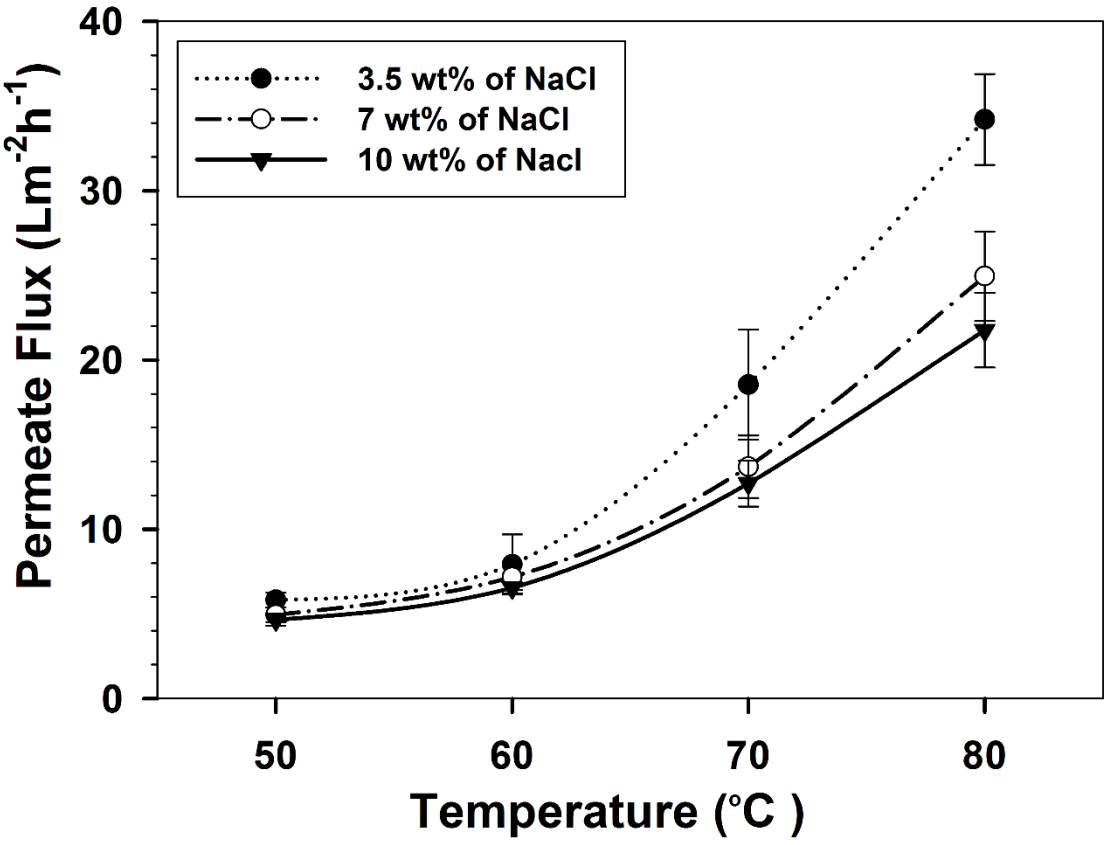


Figure 19. Effect on the feed temperature (50, 60, 70, and 80℃), Permeate (20℃) with different NaCl feed concentration (3.5, 7, 10 wt%). The feed and permeation solution flow rate (500 ml/min each).

3.3.3.2.2. Effect of feed flow rate in DCMD

The feed flow rate is one of the factors to give an effect on DCMD permeate flux. The Fig. 20 shows the feed flow effects on the permeate flux with different feed salt concentration (3.5, 7, 10 wt% of NaCl). As expected, the enhanced permeate flux was observed from Fig. 20 as increasing the flow rate in feed solution from 100ml to 500ml. The permeate flux increases as the feed flow rate increase linearly from 6.6$Lm^{-2}h^{-1}$ to 7.9 $Lm^{-2}h^{-1}$ at 3.5 wt% of NaCl concentration in feed solution at feed and permeate temperature of 60 and 20℃. The salt rejection was above 99.99% during the experiments. The permeate flux increases when the feed flow rate increase as widely reported in other DCMD studies previously (J Phattaranawik, 2001). Increasing the feed flow rate has an effects on reduction of the thickness of the temperature boundary that the temperature polarization effect become minimized. As a result, this effect enhance the sensitivity of generating the higher vapor pressure resulting in higher membrane temperature difference and greater DCMD permeate flux (M Qtaishat, 2008).

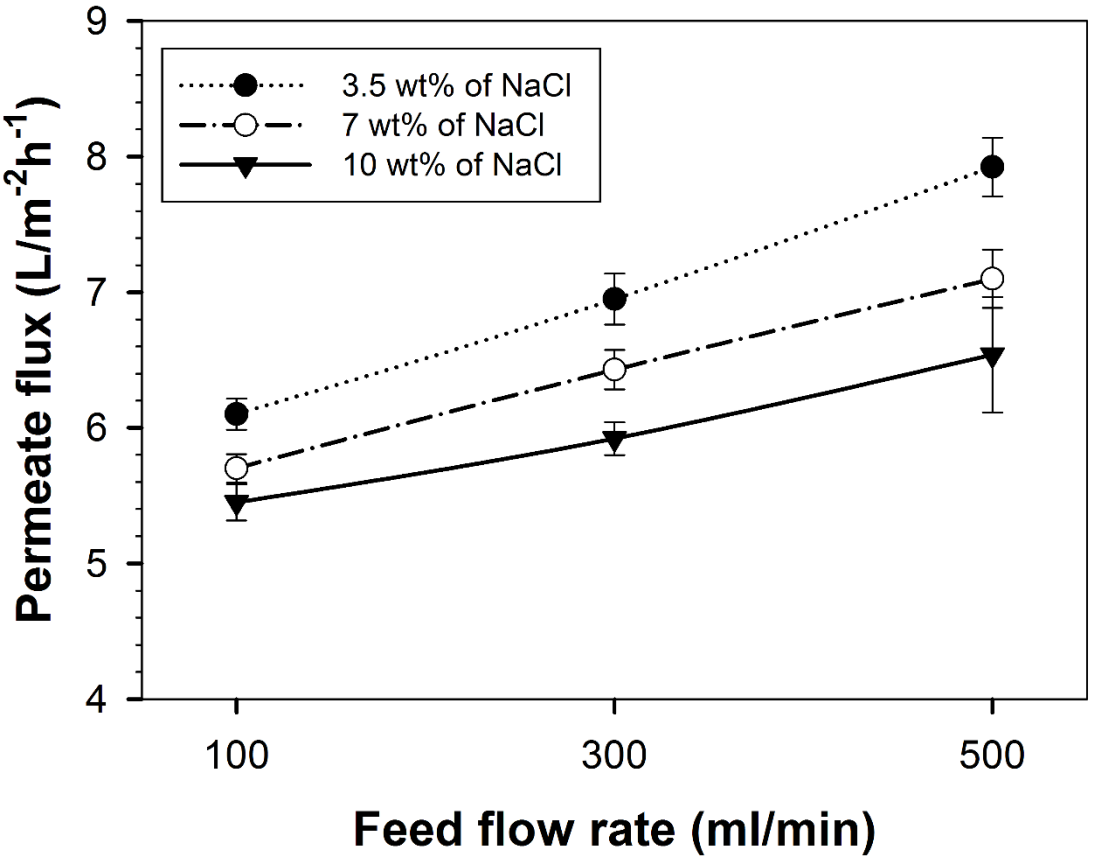


Figure 20. Effect of feed flow rate on the DCMD permeate flux (LMH) of different NaCl Feed concentration. (Feed Temperature: 60 ± 1℃, Permeate Temperature: 20 ± 1℃, Permeate solution flow rate: 500ml/min).

3.3.3.2.3 19 days of duration for DCMD performance test

Membrane wetting is a critical challenge that must consider for the industrial implementation in MD. In order to prove the membrane endurance from pore wetting, over 19 days of DCMD experiment was carried out with 3.5 wt% sodium chloride feed solution at feed and permeate temperature of 60 and 20℃. The feed and permeate flow rate were set up as 500ml/min and an initial permeate flux was obtained at 7.9 $Lm^{-2}h^{-1}$ according to Fig. 20. The Fig. 21 also illustrates that the salt rejection of NaCl does not considerably changed during the operational time. The result implies that operating PVC-g-octene membrane through the DCMD performance test proves its hydrophobicity and high wetting resistance for potential possibility of MD membranes. However, the permeate flux has slightly decreased throughout the whole experiment process. One major contributory factor seems the relatively increase the salt concentration in feed solution due to its pure water evaporation through the permeate side during the DCMD process for 19 days. Another reason could be explained that the salt crystallization might be formed and deposited on the membrane surface caused clogging the membrane surface (Gryta, 2005). The partial pore wetting might be the minor factor that reduction of permeate flux and the salt transportation occurs and such behavior was also observed as well (Gryta, 2002; P Wang, 2011).

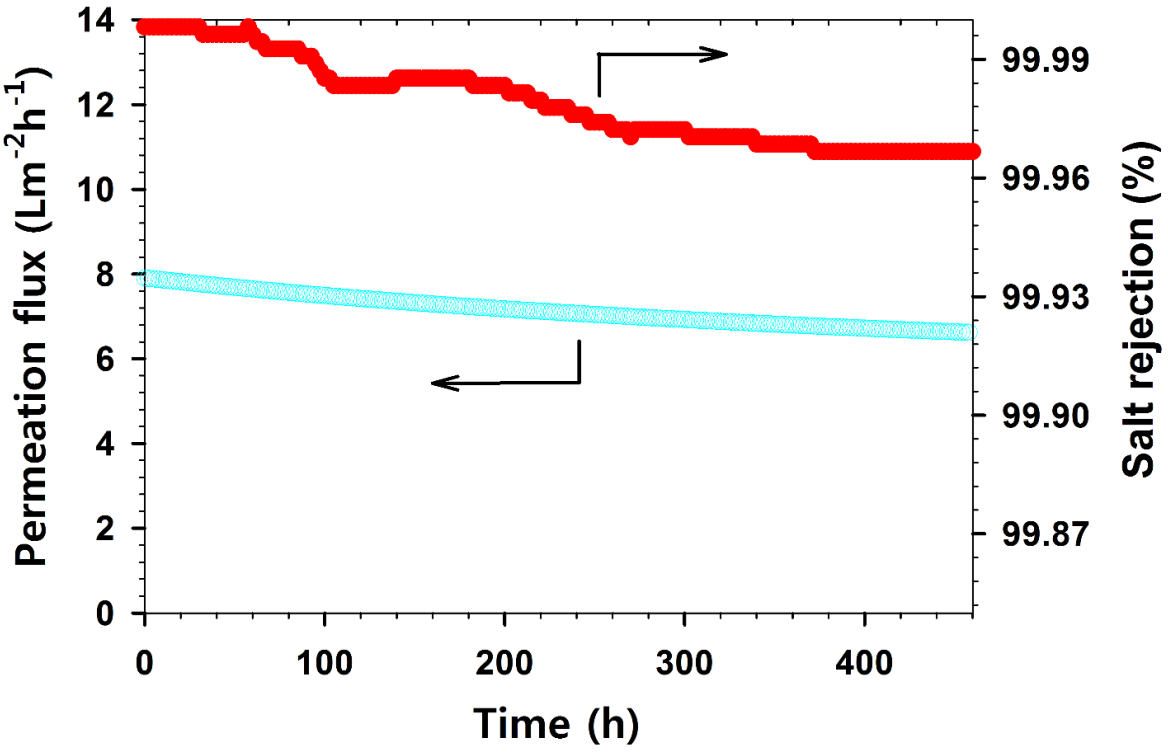


Figure 21. A long term experiment of DCMD with PVC-g-octene hollow fiber membranes; Feed and permeate temperature: 60±1 and 20±1, Feed and permeate side flow rate: 500ml/min.

Ⅳ. Conclusions

Poly vinyl chloride (PVC) was successfully modified via atom transfer radical polymerization (ATRP) in order to enhance its hydrophobicity for membrane distillation (MD) process. 1-Octene as hydrophobic monomers has been grafted on PVC backbone, resulting in enhancing from the membrane pore wettability. To confirm the successful synthesis of PVC-g-octene, XPS spectroscopy, FT-IR spectroscopy were measured after grafting of PVC-g-octene.

The synthesized hydrophobic polymers, then, prepared as dope solution with PEG to enhance the membrane pore size and porosity of the hollow fiber membrane. To obtain the high surface porosity, pore size and macrovoid free hollow fiber membranes, dual layer spinneret was applied that solvents flow through the outer channel before the dope solution immerging into the coagulation bath.

As a result, the grafted PVC-g-octene membranes increases the contact angle from 80 to 114 as a factor of higher hydrophobicity and decrease the LEVP value that indicate as a higher membrane wetting resistance. The highest pure permeation flux have attained 34.2$Lm^{-2}h^{-1}$ with highest salt rejection above 99.99% when the dope solution (PVC-g-octene/PEG-2000/NMP, 25/15/60) was used as dope solution which obtained the highest porosity as well as surface pore size and porosity.

Therefore, the preparation of a copolymer of hydrophobic 1-octene with PVC polymer having a higher hydrophobicity and proves the improvement of preventing membrane pore wetting according to LEVP and over 19days DCMD experiments. Also shows the narrow pore size distribution and low LEVP value. For improvement of, the membrane structures also plays a pivotal role to determine the permeate flux and a long term stability during the MD process.

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